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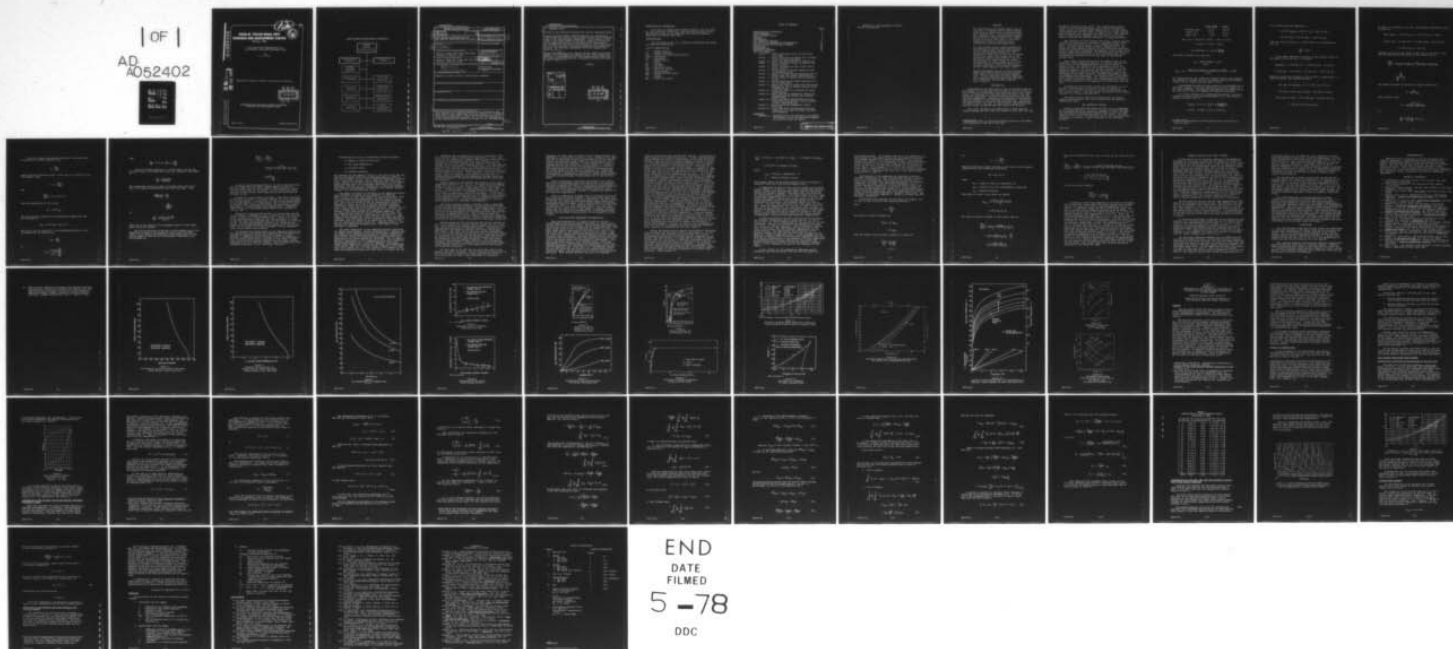
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ACID DEW-POINT DETERMINATION FOR GAS-TURBINE, WASTE-HEAT RECOVE--ETC(U)  
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Acid Dew-Point Determination  
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# DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20084

ACID DEW-POINT DETERMINATION FOR  
GAS-TURBINE, WASTE-HEAT RECOVERY UNITS

by  
B. R. Petry

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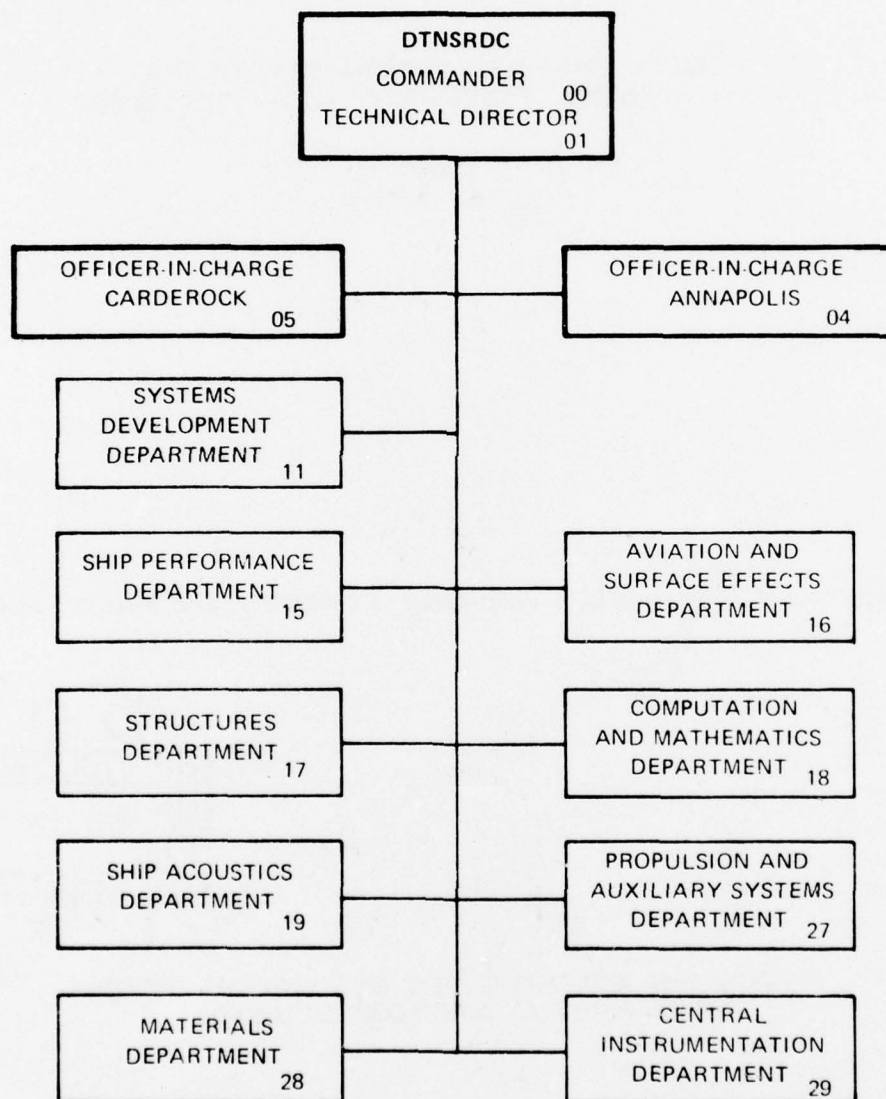
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The efficiency of gas-turbine engines can be increased at constant turbine inlet temperatures with the addition of a bottoming waste-heat recovery cycle. The waste-heat recovery unit introduces several additional problems, one of which is corrosion due to the condensation of sulfuric acid vapors in the low-temperature |  |   |

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20. ABSTRACT (Cont)

section of the waste-heat recovery unit and the downstream stack.

A review is made of past investigations into the formation of sulfur oxides and sulfuric acid in exhaust gases and the determination of the acid dew-point temperature. The influence of such items as the sulfur content of the fuel, quantity of excess air in the combustion process, and humidity of the combustion air were examined and the results are presented in such a manner that the acid dew point can be predicted for marine gas-turbine conditions. The available experimental data were compared with these results.

Exhaust characteristics of a General Electric LM2500 gas-turbine engine were investigated with respect to the acid dew-point temperature. It was concluded that the minimum surface temperature for corrosion-free operation of a waste-heat recovery unit would be 275° F (135° C).

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#### ADMINISTRATIVE INFORMATION

This work was funded under Project F43-432, Task Area SF43 432 301, Work Unit 1-2720-152. The work was performed in the Gas Turbine Branch of the Propulsion and Auxiliary Systems Department for NAVSEA (SEA 0331).

#### ACKNOWLEDGMENT

The assistance of Mr. R. K. Muench in performing this study is gratefully appreciated.

#### LIST OF ABBREVIATIONS

|       |                                   |
|-------|-----------------------------------|
| ° C   | - degree Celsius                  |
| ° F   | - degree Fahrenheit               |
| FAA   | - Federal Aviation Administration |
| ft-lb | - foot-pound                      |
| HP    | - horsepower                      |
| ° K   | - degree Kelvin                   |
| M     | - moles                           |
| max   | - maximum                         |
| mm    | - millimeter                      |
| M.W.  | - molecular weight                |
| ppm   | - parts per million               |
| ° R   | - degree Rankin                   |
| RPM   | - revolutions per minute          |
| Vol   | - volume                          |
| W     | - weight                          |
| WHB   | - waste heat boiler               |

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## ABSTRACT

The efficiency of gas-turbine engines can be increased at constant turbine inlet temperatures with the addition of a bottoming waste-heat recovery cycle. The waste-heat recovery unit introduces several additional problems, one of which is corrosion due to the condensation of sulfuric acid vapors in the low-temperature section of the waste-heat recovery unit and the downstream stack.

A review is made of past investigations into the formation of sulfur oxides and sulfuric acid in exhaust gases and the determination of the acid dew-point temperature. The influence of such items as the sulfur content of the fuel, quantity of excess air in the combustion process, and humidity of the combustion air were examined and the results are presented in such a manner that the acid dew point can be predicted for marine gas-turbine conditions. The available experimental data were compared with these results.

Exhaust characteristics of a General Electric LM2500 gas-turbine engine were investigated with respect to the acid dew-point temperature. It was concluded that the minimum surface temperature for corrosion-free operation of a waste-heat recovery unit would be 275° F (135° C).

## INTRODUCTION

Improvement in the efficiency of the gas-turbine cycle can be obtained in various ways, one of which is the use of waste-heat recovery as accomplished with bottoming cycles and recuperation. An advantage of using waste-heat recovery is that the efficiency improvement is obtained without increasing the maximum cycle temperature. However, other problems are introduced, such as corrosion in the waste-heat recovery unit. One of the corrosion problems is caused by the formation and condensation of sulfuric acid. The acid is formed in the combustion process from the sulfur introduced into the system with the fuel.

The sulfur content in the fuels used in naval ship gas-turbine engines can vary from 0.4% maximum in JP-5 fuel<sup>1</sup> to 1.3%

<sup>1</sup>Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

maximum in Navy distillate fuel.<sup>2</sup> The standard Navy marine diesel fuel,<sup>3</sup> which is generally used in gas-turbine-powered ships, can have a maximum sulfur content of 1%. In the combustion process some of this sulfur is converted to sulfur dioxide, sulfur trioxide, and ultimately to sulfuric acid. The relationship of these sulfur compounds with each other, the overall exhaust emissions and adjacent materials is summarized herein.

The formation of sulfur dioxide and sulfur trioxide has been examined for many years in relation to stationary power plants where the amount of excess air in the combustion process is small. The gas-turbine engine, however, operates with a comparatively large amount of excess air, and additional investigations are required to determine the behavior of the sulfur in the exhaust under these conditions. The present study was motivated by the various interpretations of this stationary power plant information to determine the acid dew point of gas-turbine exhaust gases.

This report reviews past work in the general area of the formation, in the combustion process, of sulfur oxides and sulfuric acid, and the determination of the acid dew point in exhaust gases. The effects of other parameters such as the amount of sulfur in the fuel, the amount of excess air in the combustion process, and humidity are also examined. Plots of analytical data are made for varying conditions to aid in the prediction of the acid dew point. Available experimental data are compared with these plots. The characteristics of an actual engine (General Electric LM2500 gas turbine) are investigated with respect to acid dew point, and a recommendation is made for the minimum temperature to be employed in a waste-heat recovery unit.

A translation from German of work by Peter Müller on acid dew point determination is included herein as appendix A. Müller's work is often referred to by other investigators and also in this report. Since an English translation is not readily available, it has been included here.

The work in this report was performed with the English system of measurements. The metric conversions are shown for temperatures only.

#### THE COMBUSTION PROCESS

Prior to discussing the effect of sulfur and its compounds in the combustion gas it will be of interest to review the chemical equations for simple combustion process in order to establish the various relationships needed in the report. For this report the air used in the combustion of the fuel was considered to consist of nitrogen, oxygen, and argon in the following amounts:<sup>4</sup>

|                            | <u>% by Volume</u> | <u>M.W.*</u> |
|----------------------------|--------------------|--------------|
| Nitrogen (N <sub>2</sub> ) | 78.03              | 28.016       |
| Oxygen (O <sub>2</sub> )   | 20.99              | 32.00        |
| Argon (A)                  | 0.98               | 39.95        |

$$\begin{aligned} \text{M.W. air} &= (28.016 \times 0.7803) + (32.0 \times 20.99) \\ &+ (39.95 \times 0.0098) = 28.97 \end{aligned}$$

$$\text{Gas constant, } R = 53.342 \frac{\text{ft-lb}}{\text{lb } ^\circ\text{R}}$$

The weight fractions (f<sub>x</sub>) then are:

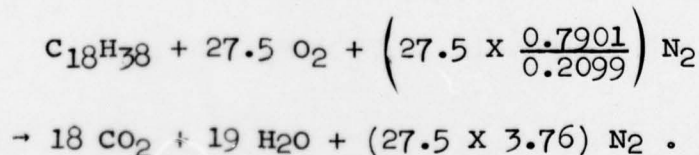
$$f_{O_2} = \frac{32 \times 0.2099}{28.97} = 0.2319$$

$$f_{(N_2 + A)} = \frac{(28.016 \times 0.7803) + (39.95 \times 0.0098)}{28.97} = 0.7681$$

For simplification, the argon and nitrogen weights were combined and treated as nitrogen so that its weight fraction then equals 0.7681, and its volume fraction equals 0.7901.

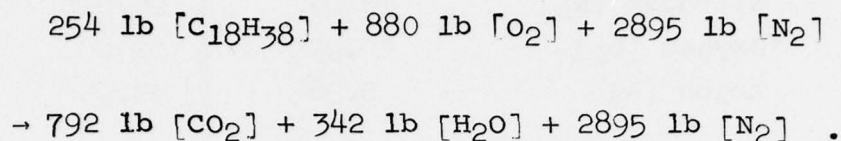
A representative fuel for this analysis was considered to be basically, C<sub>18</sub>H<sub>38</sub>. The other elements in the fuel, except sulfur, were neglected. The chemical equation for the combustion of the fuel can be used to determine the combustion products.

If we first consider 100% combustion efficiency, the sulfur content to be zero, and using stoichiometric air, the chemical equation in molar form is:



\*A list of definitions of abbreviations used in this text is given on page i.

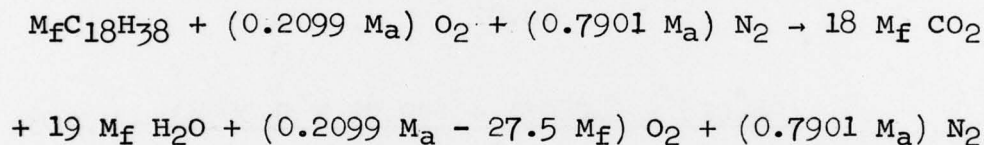
On a weight basis the equation is:



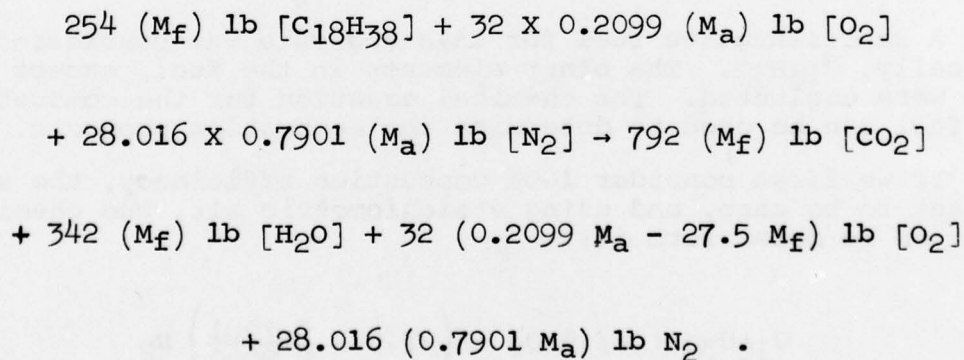
Then the air fuel ratio on a weight basis, for stoichiometric air, is:

$$\frac{W_a}{W_f} = 14.86 .$$

If the above equation is written in more general terms for any amount of air and fuel, it becomes:

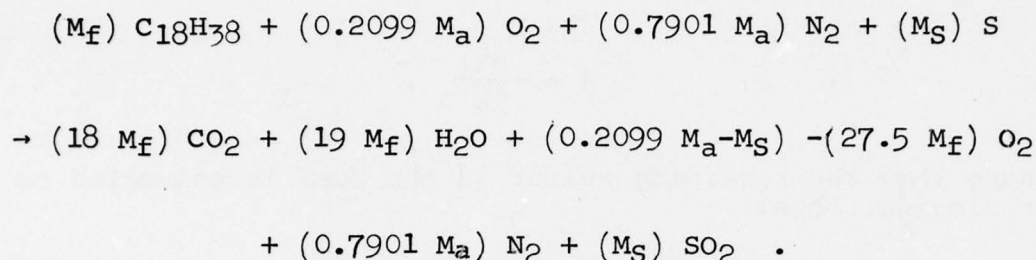


where  $M_a$  and  $M_f$  are the moles of air and fuel, respectively. In terms of weight, the equation becomes:





If sulfur is included in the fuel, the chemical equation in terms of moles is:



Assuming that all of the sulfur in the fuel is converted to  $SO_2$ , the  $SO_2$  concentration by volume in dry exhaust gas is:

$$\begin{aligned} \frac{M_{SO_2}}{M_{ed}} &= \frac{M_S}{18 M_f + 0.2099 M_a - 27.5 M_f + 0.7901 M_a} \\ &= \frac{\frac{M_S}{M_f}}{\frac{M_a}{M_f} - 9.5} . \end{aligned}$$

The amount of sulfur in the fuel or weight fraction is:

$$f_S = \frac{W_S}{W_f + W_S} .$$

Then in molar terms:

$$f_S = \frac{32.07 M_S}{254 M_f + 32.07 M_S}$$

or

$$\frac{M_S}{M_f} = \frac{7.92 f_S}{1 - f_S} \approx 7.92 f_S .$$

If we let X equal that portion of sulfur in the fuel that is converted to sulfur trioxide, then:

$$X = \frac{M_{SO_3}}{M_S} .$$

Assume that the remaining sulfur in the fuel is converted to sulfur dioxide, then:

$$1 - X = \frac{M_{SO_2}}{M_S}$$

and

$$\frac{M_{SO_2}}{M_f} = 7.92 (1-X) f_S .$$

From the composition of air we know

$$M_a = 4.76 M_{O_2} .$$

From the chemical equation for stoichiometric combustion, the air required is:

$$M_{ta} = (27.5 M_f + M_S) 4.76 .$$

The ratio,  $r_{ta}$ , of actual air in the combustion process to the stoichiometric air required is:

$$r_{ta} = \frac{M_a}{M_{ta}}$$

or

$$r_{ta} = \frac{0.2099 \frac{M_a}{M_f}}{27.5 + \frac{M_S}{M_f}} .$$

then

$$\frac{M_a}{M_f} = 4.76 r_{ta} \left( 27.5 + \frac{M_S}{M_f} \right) .$$

From the chemical equation, in weight terms, for the combustion of fuel, the weight of air per unit weight of fuel would be

$$\frac{W_a}{W_f} = \frac{28.97 M_a}{254 M_f} .$$

This expression can be set equal to the mass flow rate of air ( $\dot{m}_a$ ) in an engine divided by the fuel flow rate ( $\dot{m}_f$ ). Then

$$\begin{aligned} \frac{28.97 M_a}{254 M_f} &= \frac{\dot{m}_a}{\dot{m}_f} \\ &= \frac{\dot{m}_a}{\frac{sfc P}{3600}} \end{aligned}$$

or

$$\frac{M_a}{M_f} = \frac{3.156 \times 10^4 \dot{m}_a}{sfc P}$$

where sfc is the specific fuel consumption and P is the output power of the gas turbine.

The partial pressure of the water in the exhaust gas to the atmosphere is equal to the molecular weight ratios of these items. If we neglect the humidity in the engine inlet air and use the chemical equation for stoichiometric combustion, the relationship is:

$$\begin{aligned}
 \frac{P_{H_2O}}{P_{total}} &= \frac{M_{H_2O}}{M_{total}} \\
 &= \frac{19 M_f}{18 M_f + 19 M_f + M_a - 27.5 M_f} \\
 &= \frac{19}{9.5 + \frac{M_a}{M_f}}
 \end{aligned}$$

A plot of the variation of the air to fuel ratio with power for the General Electric LM2500 engine appears in figure 1. This plot shows that the ratio ( $\dot{m}_a/\dot{m}_f$ ) varies between 50 and 90 over the power range of the engine. At high powers the engine operates at high turbine inlet temperatures and relatively low air/fuel ratios.

Figure 2 is a plot similar to figure 1 that shows variation of the ratio of actual air to stoichiometric air ( $r_{ta}$ ) with power for the same engine. In this plot,  $r_{ta}$  varies from approximately 3.4 at high powers to 6 at idle power. The values of the ratios in figures 1 and 2 would be even higher for gas-turbine engines that operate at lower maximum cycle temperatures. Comparable values of  $r_{ta}$  for steam power plants would be on the order of 1.02 to 1.25.

Referring to previous derivations, we can see that the  $SO_2$  in the exhaust is dependent on the S content of the fuel and the ratio of actual air to stoichiometric air. Figure 3 is a plot of  $SO_2$  concentrations versus  $r_{ta}$  for various amounts of sulfur in the fuel under the assumption that all the sulfur is converted to  $SO_2$ . The  $SO_2$  concentrations decrease with increasing  $r_{ta}$  because of the proportionately greater amount of air in the process. As the sulfur in the fuel increases, the  $SO_2$  concentrations in the exhaust also increase.

The formation of sulfur oxides in the combustion process has been extensively investigated and references on this subject are included in appendix B at the end of this report. Sulfur trioxide is formed by several reactions such as the combining of  $SO_2$  with atomic oxygen which is present in the flame, or molecular oxygen which is present downstream of the flame, and the combining of SO with molecular oxygen. These reactions have been explained by Barrett, et al,<sup>5</sup> and Palmer and Beer.<sup>6</sup>



The formation of  $\text{SO}_3$  is influenced by several factors:<sup>5</sup>

- Amount of sulfur in the fuel.
- The flame temperature.
- Air/fuel ratio.
- Catalysts present.

The influence of the amount of sulfur in the fuel on the  $\text{SO}_2$  content of the exhaust gases has already been shown in figure 3. The work of Rendel, et al,<sup>7</sup> with a laboratory combustor indicates this. Their data, figures 4 and 5, show that with increasing sulfur content in the fuel, the  $\text{SO}_3$  concentration in the exhaust gases increases while the percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  decreases. Barrett, et al,<sup>5</sup> working with a laboratory combustor that provided a noncatalytic environment, show similar results, figure 6, for the concentration of  $\text{SO}_3$ .

The amount of excess air available in the combustion process also influences the amount of  $\text{SO}_3$  generated as shown by Reese, et al,<sup>8</sup> in their test results for an actual boiler. Figure 7 illustrates this relationship and shows a sharp rate of increase in the  $\text{SO}_3$  concentration at the low values of excess air. The rate of increase of the  $\text{SO}_3$  concentration levels off somewhat at excess air of 8% to 10% and increases gradually after that. These tests were conducted with fuel containing 2.0% to 2.5% sulfur and at three power settings. Barrett, et al,<sup>5</sup> show a similar trend in their work, figure 8, with a fuel containing 5 1/2% sulfur burned in a laboratory combustor. The  $\text{SO}_3$  concentrations shown in figures 7 and 8 do not agree, however, and are the reverse of what might be expected; i.e., the higher sulfur-content fuel (figure 8) gave the lower  $\text{SO}_3$  concentrations. This difference can be attributed to other factors or influences that are present in an actual boiler (figure 7) and not in a laboratory burner (figure 8). Comparing figure 4, also derived from laboratory combustor data, with figure 8, good agreement is apparent.

The flame temperature in the combustion process influences the amount of  $\text{SO}_3$  formed. Several investigators<sup>7-9</sup> indicate that the higher flame temperature and also higher metal temperatures are conducive to increased  $\text{SO}_3$  formation. Boilers operated at above design ratings can accelerate the formation of  $\text{SO}_3$  while operation at part loads reduces the formation. This is shown in figure 7 where Reese, et al,<sup>8</sup> reported on three load conditions. The exact mechanism of the increased formation of  $\text{SO}_3$  with higher flame temperatures is not well defined. One explanation<sup>5</sup> would be that there is a reaction of  $\text{SO}_2$ , produced in the flame, with atomic oxygen ( $\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$ ) which is also present in the flame and immediately beyond the flame front, to produce the  $\text{SO}_3$ .

Catalysts play an important part in the formation of  $\text{SO}_3$ . The reaction of  $\text{SO}_2$  with molecular oxygen ( $\text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{SO}_3$ ) would, in the absence of a catalyst, proceed very slowly and produce only an insignificant amount of  $\text{SO}_3$ . However, in the presence of an active catalyst, this reaction can occur very rapidly and form objectional amounts of  $\text{SO}_3$ .<sup>5</sup> This reaction, for the most part, takes place in the cooler regions of the system<sup>10</sup> where it will adversely affect the waste-heat recovery unit. Many materials will act as catalysts, some of which are generated in the combustion systems. These materials range from vanadium oxides, where the vanadium is introduced with the fuel, to nitrous oxides, produced by the combustion process, and to ferrous oxides found in the gas-turbine engine and the waste-heat recovery unit.

Sulfur trioxide in the exhaust gas exists as a dry vapor at temperatures above  $600^\circ \text{F}$  ( $315^\circ \text{C}$ ). At temperatures of approximately  $300^\circ$  to  $400^\circ \text{F}$  ( $149^\circ$  to  $204^\circ \text{C}$ ), there is association of sulfur trioxide and water to form sulfuric acid ( $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ ). Varying degrees of association exist between  $300^\circ$  and  $600^\circ \text{F}$  ( $149^\circ$  to  $315^\circ \text{C}$ ).<sup>8</sup> The sulfuric acid is, of course, in a vapor state at temperatures above the dew point. In the vapor state, the sulfuric acid has little or no effect on the materials in the exhaust system;<sup>10</sup> however, when it condenses severe corrosion problems exist. An accurate determination of the dew-point temperature is, therefore, very important.

The sulfur trioxide content of exhaust gases is monitored closely in steam generating plants and large quantities of data on this subject have been reported. Such plants operate with low excess air and even approach stoichiometric combustion. Operation with 1% and less excess air has been achieved, and the maximum value is approximately 25%. This is done not only for increased efficiency but also to reduce or practically eliminate the formation of sulfur trioxide. Figure 7 shows how rapidly the formation of sulfur trioxide increases with additional excess air.

Similar quantities of test data for the sulfur trioxide content of the exhaust gas from gas-turbine engines are not available. The testing of gas-turbine engine exhaust gases has so far been conducted primarily on aircraft engines. Slusher<sup>11</sup> of FAA reported test data from the operation of a Pratt and Whitney TF30 engine. The fuels used in the many aircraft applications have a low sulfur content, and because of this, the sulfur oxides in the exhaust are low and are not measured. Sometimes the sulfur oxides are calculated from the sulfur content in the fuel, and frequently they are ignored completely. The shaft power version of the gas-turbine engine, which is used in ships and stationary power plants, is operated with fuels that have higher sulfur content and the sulfur oxide emissions are then larger and become more important.

The fuel used in the FAA test was Jet-A fuel, and it contained 0.05% sulfur by weight. The  $\text{SO}_3$  and  $\text{SO}_2$  concentrations in the exhaust were 0.2 ppm and 1.45 ppm, respectively, giving a ratio of  $\text{SO}_3/\text{SO}_2$  of 13.8%. This percentage is in general

agreement with data shown in figure 5 even though Slusher's was obtained at a much larger excess air value. Slusher's data show that 44% of the sulfur in the fuel was converted to  $\text{SO}_2$  and 6% to  $\text{SO}_3$ ; the remaining sulfur passed out of the exhaust in the form of sulfates and sulfides. If this information is used in conjunction with data shown later in the report, it indicates that the acid dew point would be approximately  $200^\circ \text{F}$  ( $93^\circ \text{C}$ ). This temperature may seem low, but it must be remembered that the sulfur content of the fuel was extremely low. Additional trials should be conducted on gas-turbine engine exhaust gases to accumulate a representative quantity of sulfur oxide emission data which should provide a better prediction of the acid dew point.

Since contaminants in the fuels and oxides in the various parts of the gas-turbine engine and exhaust duct can influence the sulfur trioxide formation, the tests should be performed in a realistic installation. In fact, measurements should be made in a waste-heat boiler installation of various materials since ferric oxide is an important catalyst in forming  $\text{SO}_3$  from  $\text{SO}_2$  at the lower gas temperatures.

Figure 9 summarizes available data on conversion of the sulfur in the fuel to sulfur trioxide. The data points shown were determined from trials by several investigators. The data points at the low air ratios are from steam boiler plants where many measurements have been made. Only a small portion of these data is shown in figure 9. The single data point at 4.3 air ratio is from Slusher's<sup>11</sup> test on an aircraft engine. This plot again points out the lack of data at the higher air ratios, and additional data are required to establish this relationship firmly so that the waste-heat recovery units can be designed with confidence.

#### ACID DEW-POINT TEMPERATURE DETERMINATION

Many investigators over the past 50 years or so have studied means of measuring  $\text{SO}_3$  concentrations in exhaust gases and the associated acid dew point. As previously indicated, the greater part of this work has been done in conjunction with steam power plants which run at a relatively low excess air level. Early investigators were aware of the effect of a trace of sulfuric acid vapor in the combustion gas on the dew point. Also, the electrical conductivity of acid condensate was much greater than pure water condensate. The early dew-point meters were then electrical devices which measured the temperature at which electrical continuity between two electrodes was established. This type of dew-point meter is still produced today. After the development of the electric type of dew-point meter, practical chemical procedures were developed for determining the  $\text{SO}_3$  content of combustion gas. Since there is a relationship between the acid dew point and the sulfuric acid concentration in the combustion gases, this procedure can be used for determining the dew point. These methods absorbed the  $\text{SO}_3$  in an isopropyl



alcohol solution and then analyzed the solution. This process is time consuming and limited in accuracy. A wide discrepancy also existed between the various investigators of the acid dew point, whether using electrical or chemical methods as shown in figure 10. This plot was first published by Müller<sup>12</sup> who used thermodynamic relationships for calculating the dew points of flue gases with low sulfuric acid concentrations. A translation of Müller's article is included in this report as appendix A. Some of the test data are in fair agreement with the analytical work while other data deviate as much as 176° F (80° C) for the dew-point temperature at low concentrations of H<sub>2</sub>SO<sub>4</sub>. If a steam boiler is operated in a manner to take advantage of the apparent lower dew-point temperature, severe corrosion problems could be encountered. Müller's analytical expression is now generally accepted as being the most accurate value of dew-point temperature with respect to sulfuric acid concentrations. In fact, one journal article<sup>8</sup> states that the most accurate method of determining acid dew point is through measuring the H<sub>2</sub>SO<sub>4</sub> concentration in the flue gas and using Müller's correlation. Several investigators<sup>13,14</sup> have, through careful laboratory experiments, produced experimental results that are in agreement with Müller's work. The method used was an equilibrium vapor pressure determination at various temperatures and sulfuric acid concentrations. In this method a gas containing a known quantity of sulfuric acid is passed through a condenser which is held at a specific temperature. After a known volume of gas is passed, the sulfuric acid that is condensed is washed out with an isopropyl alcohol solution and analyzed. The amount of acid that was not condensed can then be determined and is a measure of the partial pressure of the H<sub>2</sub>SO<sub>4</sub> at the condenser temperature. This partial pressure represents the H<sub>2</sub>SO<sub>4</sub> concentration corresponding to a dew point of that temperature. Lisle and Sensenbaugh have explained the above method in their paper<sup>13</sup> and have compared their results with Müller's analytical work in figure 11. As can be seen, the experimental laboratory data are in very close agreement with the analytical work. This method of dew-point determination can be used to measure the dew point in actual installations. However, it would be time consuming, and care must be taken in designing the probe to prevent condensation, reaction, or absorption of the acid within it.

Verhoff and Banchemo have reviewed the problem of predicting acid dew points and the work of other investigators.<sup>15</sup> In contrast with the work of Müller they state that "An accurate thermodynamic prediction of dew point appears impossible at the present time and, because it is important to be able to predict the dew point of flue gases, an empirical correlation of the experimental data of dew point as a function of the sulfuric acid and water vapor pressures would be desirable." By utilizing equations and test data developed by other investigators, Verhoff and Banchemo developed a formula for the dew-point temperatures with respect to the partial pressures of sulfuric acid and water. Their formula is:



$$\frac{1}{T_{DP}} = 0.002276 - 0.00002943 \ln (pH_2O) - 0.0000858 \ln (pH_2SO_4) \\ + 0.00000620 (\ln pH_2SO_4)(\ln pH_2O)$$

where

$T_{dp}$  = dew-point temperature, °K

$p$  = partial pressure, mm Hg.

This formula gives values which generally agree with Müller's analytical work and is relatively simple to use.

A comparison of Müller's data and the Verhoff and Banchero formula appears in figure 12. Air ratios varying from stoichiometric to four times stoichiometric were used in plotting the Verhoff and Banchero formula. The Müller data are calculated for stoichiometric conditions. The figure shows that in a range of dew-point temperatures of 200° to 400° F (93° to 204° C) the Verhoff and Banchero formula gives lower values at the low dew points and higher values at the high dew points for the stoichiometric condition. The crossover point is at 230° F (110° C). The plot also shows that for a full power air ratio and a range of temperatures (250° to 300° F) (121° to 149° C) that are of most interest to the waste-heat boiler program, the Verhoff and Banchero dew points are approximately 8° lower than Müller's. The increased air or higher air ratios in the combustion process have a diluting effect on the sulfur trioxide concentration, thereby giving lower dew-point temperatures.

Verhoff and Banchero used data from several investigators for dew-point temperatures which varied from 212° to 446° F (100 to 230° C). Their formula does not fit any one set of data completely. However, the deviations are generally less than 12° F (6.7° C) from the test data. These differences indicate that variations in test conditions and inaccuracies of data exist to the extent that the dew-point temperatures are not firmly defined. The vapor-liquid characteristics of the  $H_2SO_4/H_2O$  system are such that the first drop of  $H_2SO_4$  to condense is a highly concentrated acid. A heat exchanger that is designed to operate close to the dew-point temperature must then give careful consideration to the prediction of this temperature. In determining the dew-point temperature, the Verhoff and Banchero correlation is easier to use than Müller's graphical data. It will, therefore, be used for the remainder of the report.

A plot, figure 13, was produced by combining several parameters that are associated with the acid dew point of a

gas-turbine exhaust. The formulas derived in the combustion process section of this report and the dew point/partial pressure relationship developed by Verhoff and Banchero<sup>15</sup> were used to develop this figure. It is configured to allow the determination of the dew point if the fraction of  $\text{SO}_3$  in the exhaust gas to sulfur in the fuel, and the ratio of actual air to theoretical air is known. As an example, if 2 1/2% of the sulfur in a 1% sulfur fuel is converted to  $\text{SO}_3$  ( $X = 0.01$ ) in an engine operating at an actual to theoretical air ratio of 4, the acid dew point would be 243° F (117° C).

The humidity of the combustion air influences the acid dew-point temperature and must be considered for the determination of this temperature. The effect of the humidity is to dilute the acid vapor which then slightly reduces the dew-point temperature increment (acid dew-point temperature -  $\text{H}_2\text{O}$  in exhaust dew-point temperature) as shown in Müller's data, figure 10. The partial pressure of the water in the exhaust is increased by the humidity and results in a significantly higher water saturation temperature, more than offsetting the slight change in the dew-point temperature increment noted above. The net effect of increased humidity is always to increase the acid dew-point temperature.

To determine the magnitude of the effect of humidity, let us refer to the section on the combustion process.

Then

$$X = \frac{M_{\text{SO}_3}}{M_S} .$$

The weight of sulfur trioxide is:

$$W_{\text{SO}_3} = 80 M_{\text{SO}_3}$$

$$= 80 M_S X .$$

Then the weight ratio of sulfur trioxide to sulfur is:

$$\frac{W_{\text{SO}_3}}{W_S} = \frac{80 M_S X}{32 M_S}$$

$$= 2.5 X$$

or

$$x = 0.4 \frac{w_{SO_3}}{w_s} .$$

The relationship of sulfur trioxide to the water in the incoming combustion air can be derived as follows:

$$w_w = w_{as} r_{ta} h_s$$

where

$w_w$  = weight of water in combustion air

$w_{as}$  = weight of air for stoichiometric conditions

$h_s$  = specific humidity.

Then moles of water in the inlet air equals:

$$M_{H_2O} = \frac{14.86 M_f 254 r_{ta} h_s}{18}$$

$$= 209.7 M_f r_{ta} h_s .$$

The ratio of sulfur trioxide to total water then is:

$$\frac{M_{SO_3}}{M_{H_2O}} = \frac{x M_s}{19 M_f + 209.7 M_f r_{ta} h_s}$$

$$= \frac{x}{19 + 209.7 r_{ta} h_s} \frac{M_s}{M_f}$$

$$= \frac{7.92 x f_s}{19 + 209.7 r_{ta} h_s} .$$

The partial pressure of the water in terms of the total gas flow is:

$$\frac{P_{H_2O}}{P_{total}} = \frac{M_{H_2O}}{M_{total}} = \frac{19 M_f + 209.7 M_f r_{ta} h_s}{18 M_f + 19 M_f + M_a - 27.5 M_f + 209.7 M_f r_{ta} h_s}$$

$$= \frac{19 + 209.7 r_{ta} h_s}{9.5 + 209.7 r_{ta} h_s + \frac{M_a}{M_f}}$$

or for zero inlet humidity

$$\frac{P_{H_2O}}{P_{total}} = \frac{19}{9.5 + \frac{M_a}{M_f}} .$$

In order to realize the magnitude of the effect of humidity, let us then take a case where 1.0% sulfur content fuel is used with an air ratio of 3.4 and an ambient temperature of 100° F (38° C). A realistic figure for the conversion of sulfur into sulfur trioxide in the combustion process is 6% by weight. If this value is used with a 70% relative humidity ( $h_s = 0.03$ ), the partial pressure,  $p_{SO_3} / p_{H_2O}$ , equals  $4.71 \times 10^{-5}$ . With a 0% relative humidity, this ratio is  $1.0 \times 10^{-4}$ . At an air ratio of 6 the partial pressure ratio would be  $3.3 \times 10^{-5}$  for the 70% humidity and  $1.0 \times 10^{-4}$  for zero humidity. Plotting these values on figure 14 reveals that the effect of humidity is to increase the dew-point temperature, in this case approximately 12° F (6.7° C) for the air ratio of 3.4. Figure 14 is similar to figure 13 but shows only the lines of two air ratios for specific humidities of 0.0 and 0.03. The data for this plot were generated from Verhoff and Banchero's correlation for a 1% sulfur fuel and a  $SO_3$  conversion of 6% by weight ( $X = 0.024$ ). The increase of dew-point temperatures at low power settings (or high air ratios) is even greater than at the low air ratios. For an air ratio of 6 this dew-point temperature increase is approximately 19° F (10.5° C). This is due to the additional moisture brought into the system with the higher excess air which in turn raises the dew point. This example shows that humidity cannot be neglected in the design of a WHB.



## EXHAUST EVALUATION FOR LM2500 ENGINE

An application of the dew-point temperature determination developed in this study was made for the LM2500 gas turbine to determine the conditions which would be encountered in the actual installation of a waste-heat boiler. Since the humidity of the engine inlet air has considerable effect on the dew-point temperature, some of the available data were reviewed in order to determine realistic ambient humidity limits for this study. Humidity conditions at sea vary appreciably with location and time of year. For instance, areas in the Persian Gulf rarely exceed 70% relative humidity with an average being 55%, while in the North Sea relative humidities are 70% to 90% at ambient temperatures of approximately 60° F (15.6° C).<sup>16</sup> It was decided to use specific humidity (lb H<sub>2</sub>O/lb dry air) for the application study rather than relative humidity, thereby eliminating temperature from the calculations. The range of specific humidity selected for this work is 0 to 0.03 lb H<sub>2</sub>O/lb dry air. The 0.03 lb H<sub>2</sub>O/lb dry air figure corresponds to relative humidities of approximately 70% at 100° F (38° C) ambient and 100% at 90° F (32° C) ambient temperature which appears to be a realistic maximum. Relative humidities of 100% do exist at sea, especially during rainstorms, but 100% relative humidity with 100° F (38° C) ambient temperature is most likely never encountered.

The fuel used in this case has the same composition as that used in the combustion process section. The maximum sulfur content of the available fuels varies from 0.4% for JP-5<sup>1</sup> to 1.3%<sup>2</sup> for naval distillate. The value used in this case is 1.0% sulfur. This figure is the same as the maximum allowed in the U. S. Navy Marine Diesel Fuel oil specification.<sup>3</sup> It is expected that the present fuel or energy crisis will cause a gradual decrease in the fuel quality so that the 1.0% sulfur content will soon be a reality.

As discussed previously, an analysis of the exhaust gas composition from stationary power plants and one gas-turbine engine indicate that approximately 6.0% by weight ( $X = 0.024$ ) of the sulfur in the fuel is converted to sulfur trioxide.<sup>8,11</sup> Recent information from Environmental Protection Agency personnel at Research Triangle Park, North Carolina, indicates that 10% by weight ( $X = 0.04$ ) conversion of the sulfur in the fuel to sulfur trioxide is not uncommon. The study was, therefore, performed with "X" values varying from 0.024 to 0.04.

The dew-point temperature analysis for the LM2500 gas turbine was made within the above limits and for engine operating conditions of full power and idle. The data for these conditions are plotted in figure 15 and show the variation of dew-point temperatures with specific humidity, sulfur conversion amounts ( $X$ ) and engine power level. At full power the air ratio,  $r_{ta}$ , equals 3.4, and at idle,  $r_{ta}$  equals 6. The lines of zero specific humidity are identical to the lines of constant air ratio in figure 13. The figure 13 data do not account for any moisture in

the engine inlet air. In figure 15 it can easily be seen how increased humidity elevates the dew-point temperature. The dew-point temperature at full power with a specific humidity of 0.03 lb H<sub>2</sub>O/lb dry air and a sulfur conversion amount of  $X = 0.04$  is 269° F (132° C). This may be an extreme condition in that the relative humidity would be at least 70% at 100° F (38° C) ambient temperature, and the sulfur conversion amount is possibly high but realistic for an upper limit. As mentioned previously, additional test work is required to better define the amount of conversion of sulfur in the fuel to sulfur trioxide in gas-turbine engine exhausts.

The data plotted in figure 15 also show clearly how the humidity affects the dew-point temperature. An increase in the humidity from 0 to 0.03 lb H<sub>2</sub>O/lb dry air gives approximately a 12° F (6.7° C) increase in the dew-point temperature when at maximum power and an even greater increase, 19° F (10.5° C), at idle power. The plot for full power is similar to the plot for idle power except for the greater temperature span at idle. The development program for a waste-heat boiler should include the effect of humidity conditions in order to produce a successful design.

The study shows that the minimum operating surface temperature of a waste-heat boiler should be 275° F (135° C) to prevent acid condensation for normal operating conditions. Extremely high humidities along with high ambient temperatures and high-power operation would give even higher acid condensation temperatures. The walls of the exhaust systems perhaps should be operated at a somewhat higher temperature than the boiler if there is any amount of fouling present. The fouling deposits on low-temperature surfaces are acidic in nature and often are damp and hygroscopic which is very undesirable.<sup>8</sup> The fouling deposits also increase the boundary layer thickness which lowers the gas velocity near the wall surface. The lower velocities favor the formation of sulfur trioxide, especially near catalytic particles and surfaces as iron oxides (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>).<sup>17</sup>

#### CONCLUSIONS

The acid dew point study has reviewed methods for predicting the dew-point temperature of exhaust gases and has provided some insight into the formation of sulfur trioxide in the exhaust system. This study concludes that waste-heat boilers for gas-turbine engines should be designed to operate at a surface temperature of no less than 275° F (135° C) if the condensation of sulfur acid and serious corrosion is to be avoided.

Any corrosion problems resulting from operating temperatures below the acid dew point must be carefully weighed. Tradeoff studies addressing such things as corrosion rate or useful life of a waste heat boiler, power settings, length of time at various powers, fuels specified, possible use of additives, and costs may be required to resolve such problems.

## RECOMMENDATIONS

Additional work is required in the acid dew-point area in order to accumulate a representative amount of data on gas-turbine installations similar to what is available for steam plants. Data are particularly needed for the amount of conversion of the sulfur in the fuel to sulfur trioxide at high excess-air levels. Only one applicable data point was found in the literature. Since the amount of excess air present influences this conversion value, steam-boiler data are not completely applicable.

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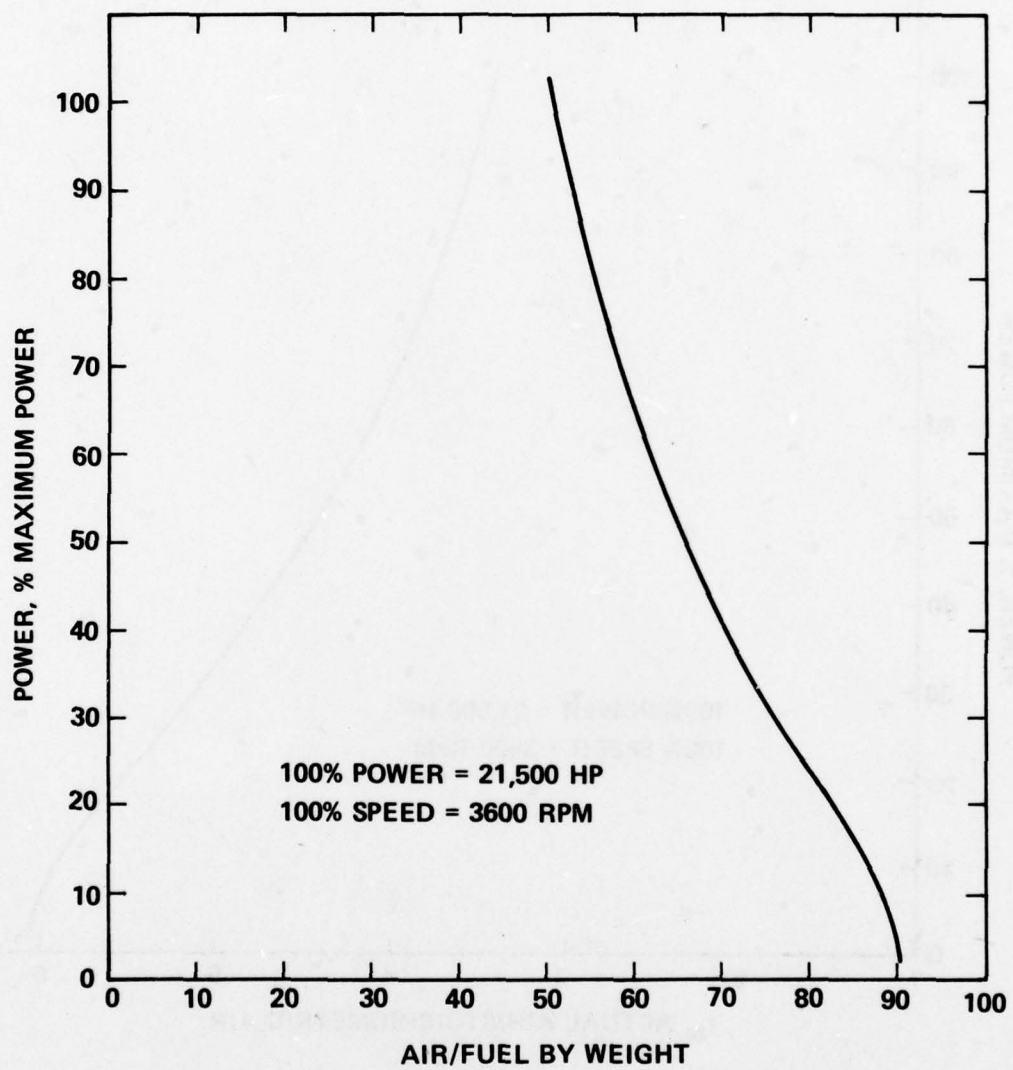


Figure 1  
Variation of Air to Fuel Ratio with Power  
LM2500 Engine, Cubic Load Line

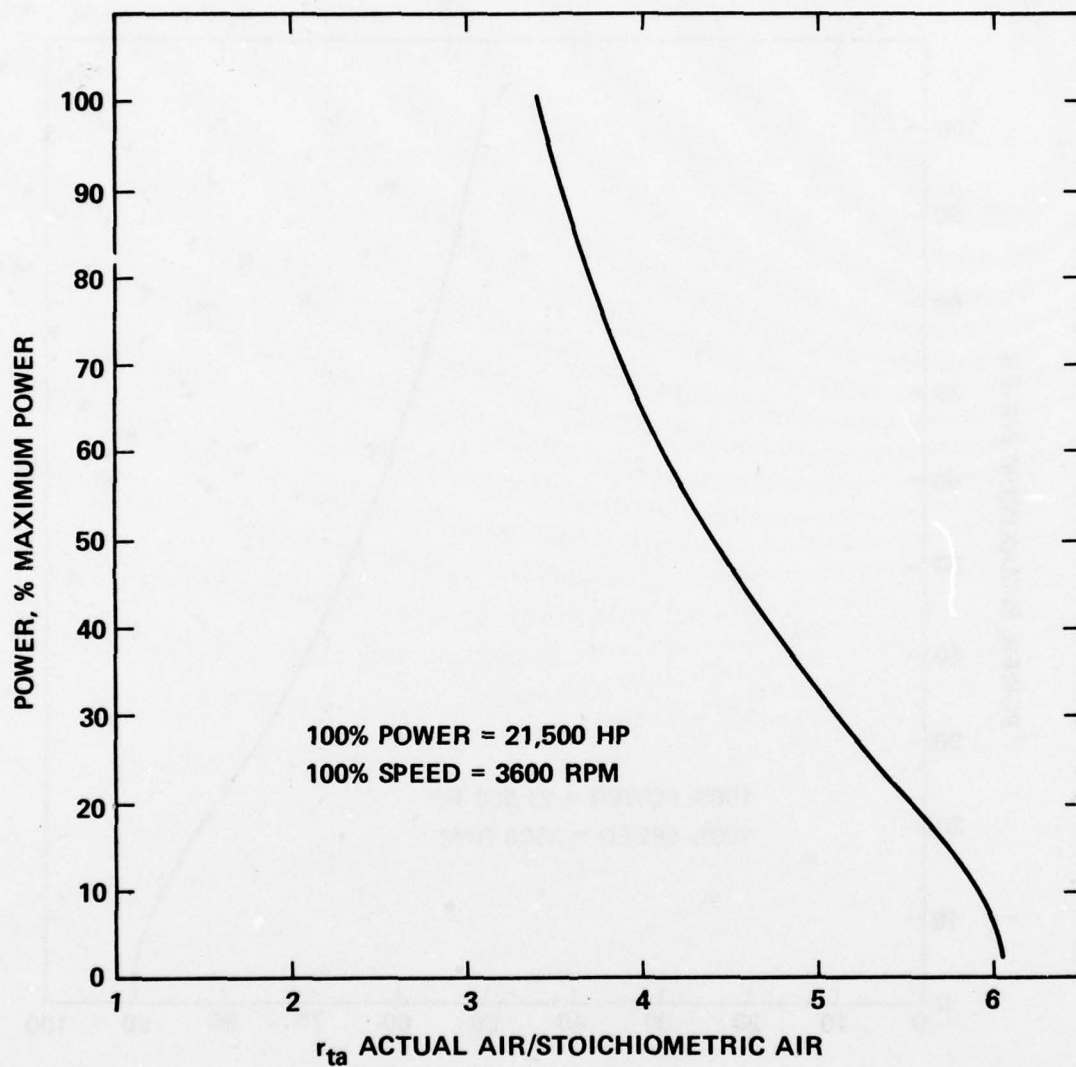


Figure 2  
Variation of Actual Air to  
Theoretical Air Ratio with Power  
LM2500 Engine, Cubic Load Line

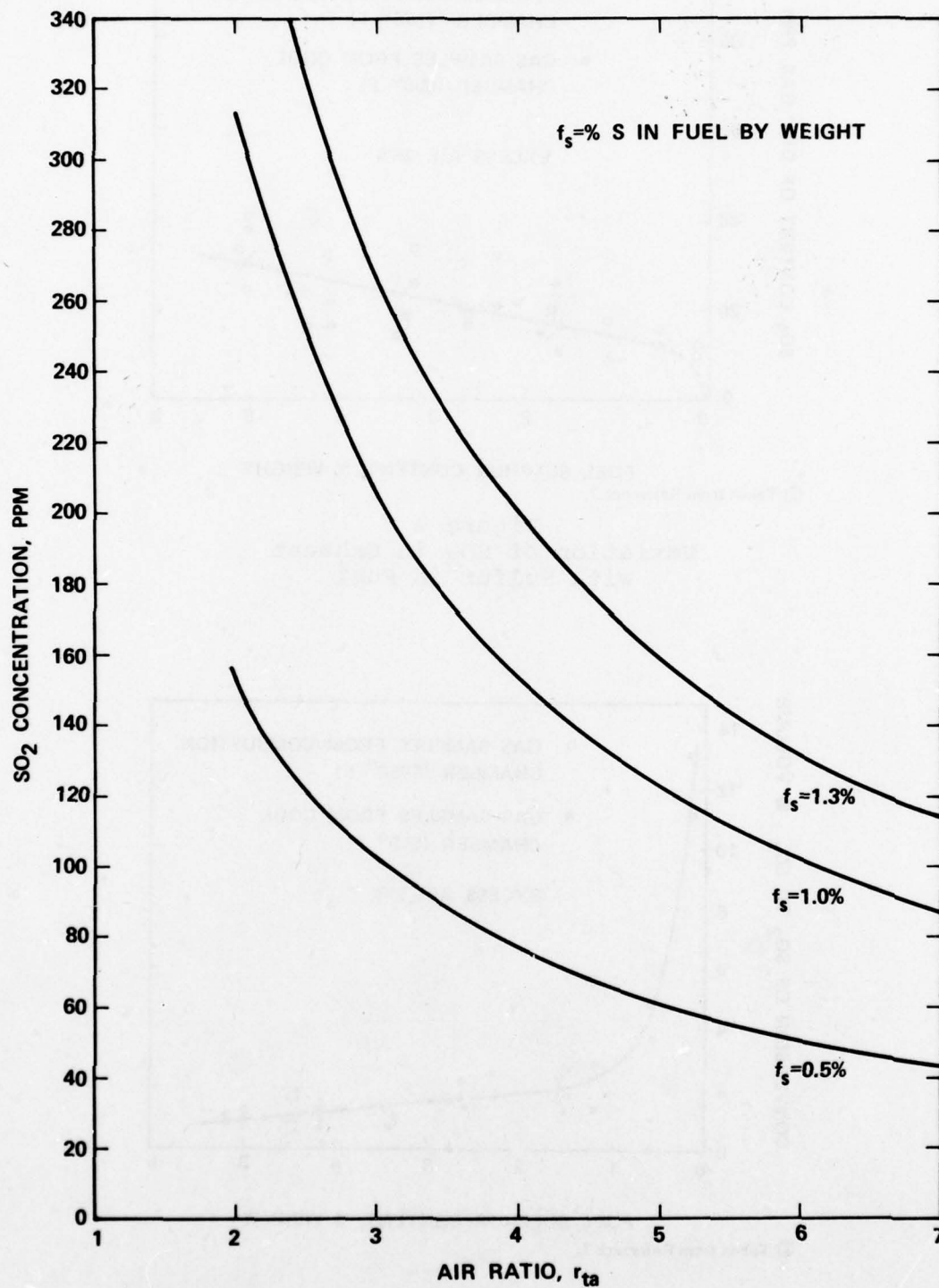
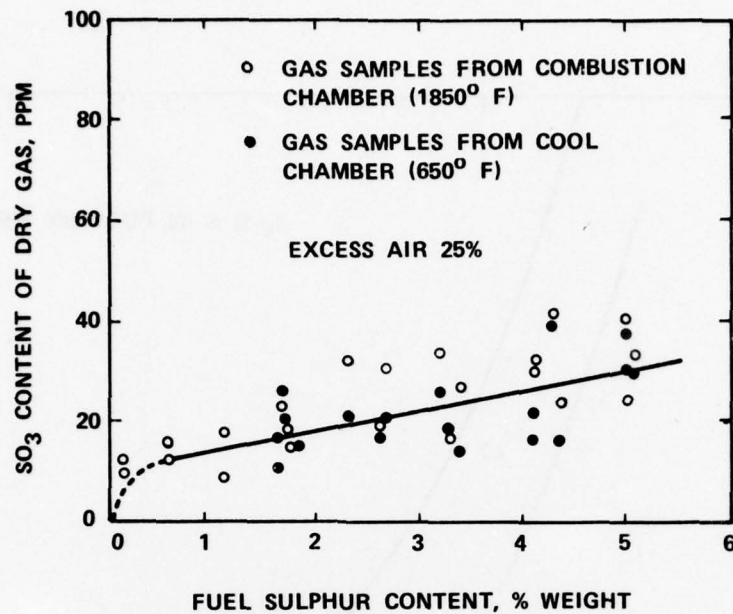
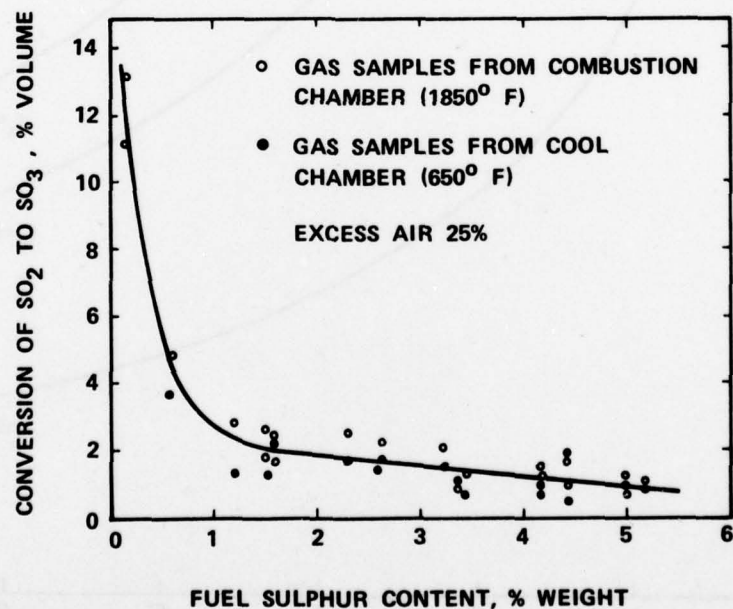


Figure 3  
 $SO_2$  Concentration in Exhaust Gas  
 $X = 0$



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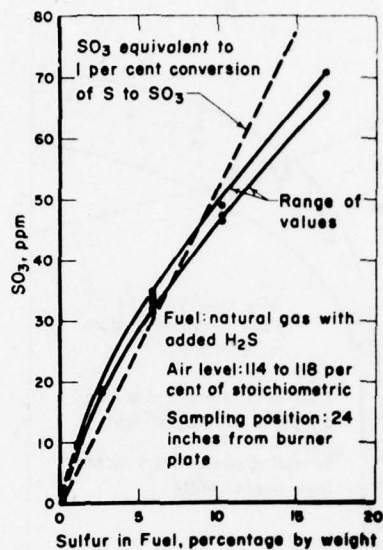
Figure 4  
Variation of SO<sub>3</sub> in Exhaust  
with Sulfur in Fuel



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Figure 5  
Conversion of SO<sub>2</sub> to SO<sub>3</sub>  
versus Sulfur in Fuel





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Figure 6  
Effect of Sulfur  
Content of Fuel on  
Formation of SO<sub>3</sub>

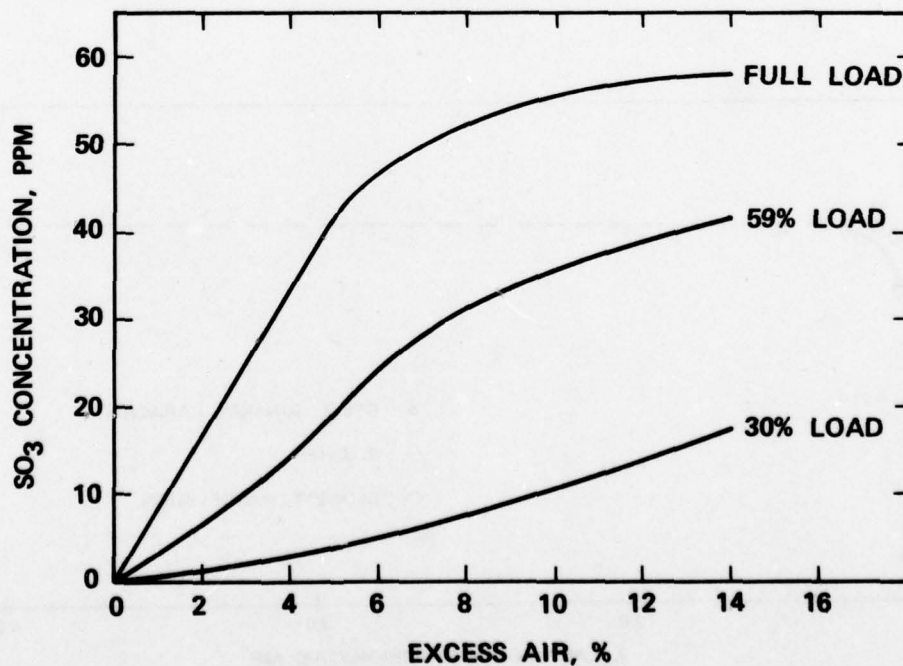
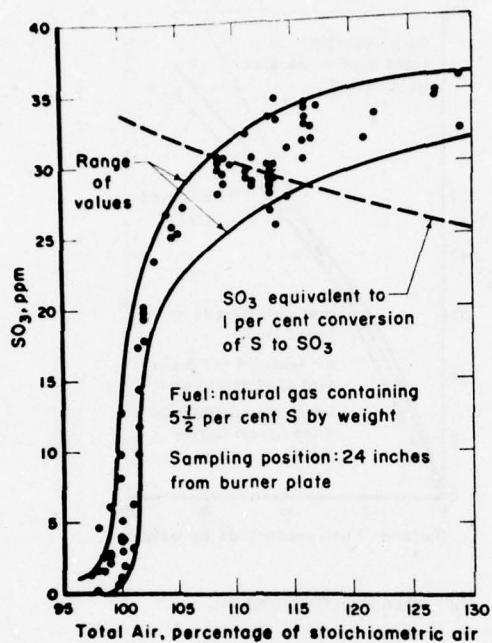


Figure 7  
Variations of SO<sub>3</sub> Concentrations  
with Excess Combustion Air



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Figure 8  
Effect of Excess Air  
on Formation of  $\text{SO}_3$

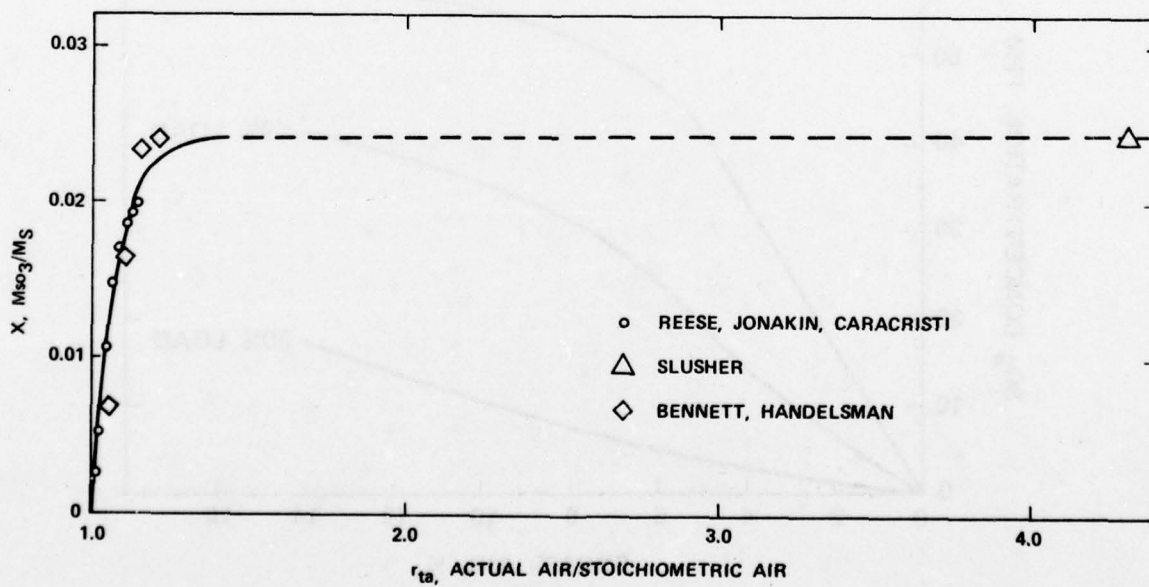
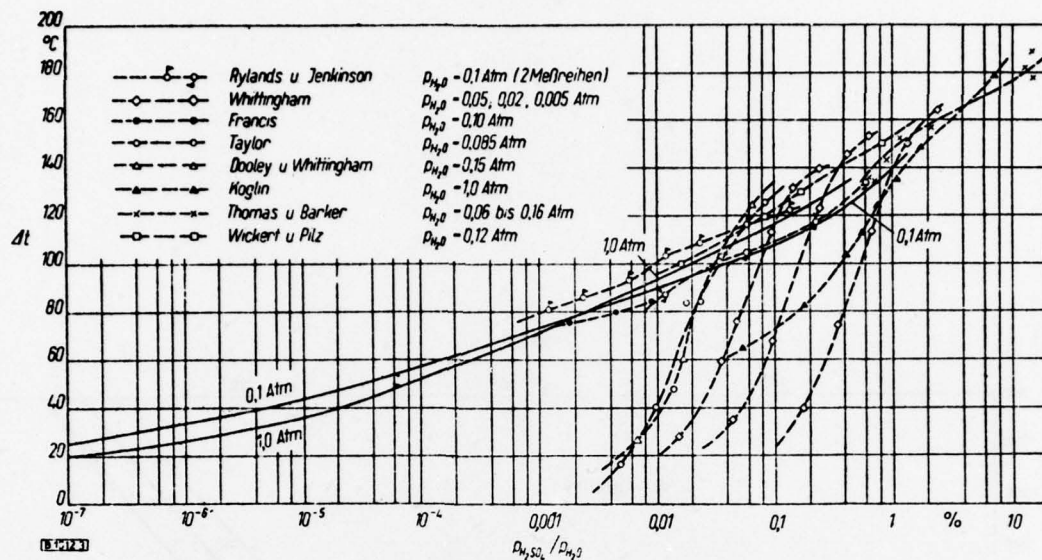
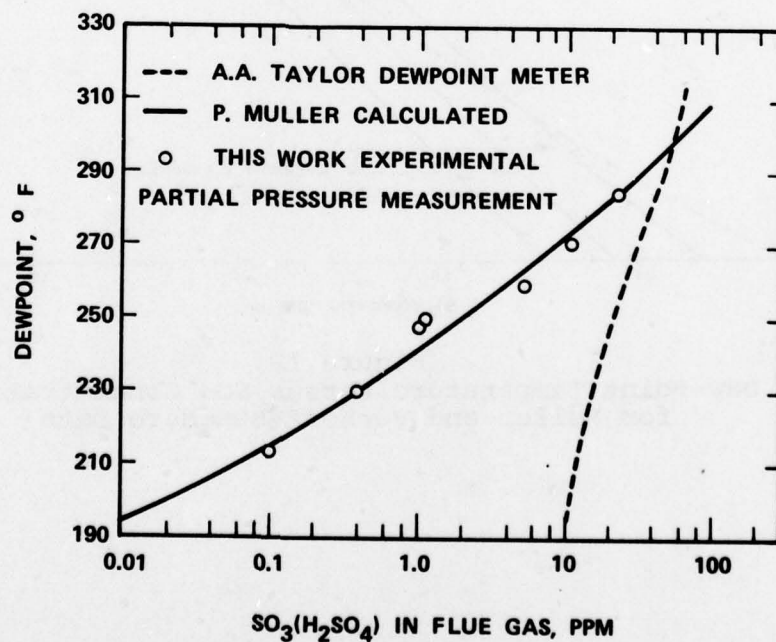


Figure 9  
Variation of Sulfur Conversion  
to  $\text{SO}_3$  with Air Ratio



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Figure 10  
Dew Point  $\Delta t$  Above Water Saturation Temperature  
versus Partial Pressure Ratio of  $H_2SO_4$  to  $H_2O$



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Figure 11  
Dew Point as a Function  
of  $H_2SO_4$  Concentration

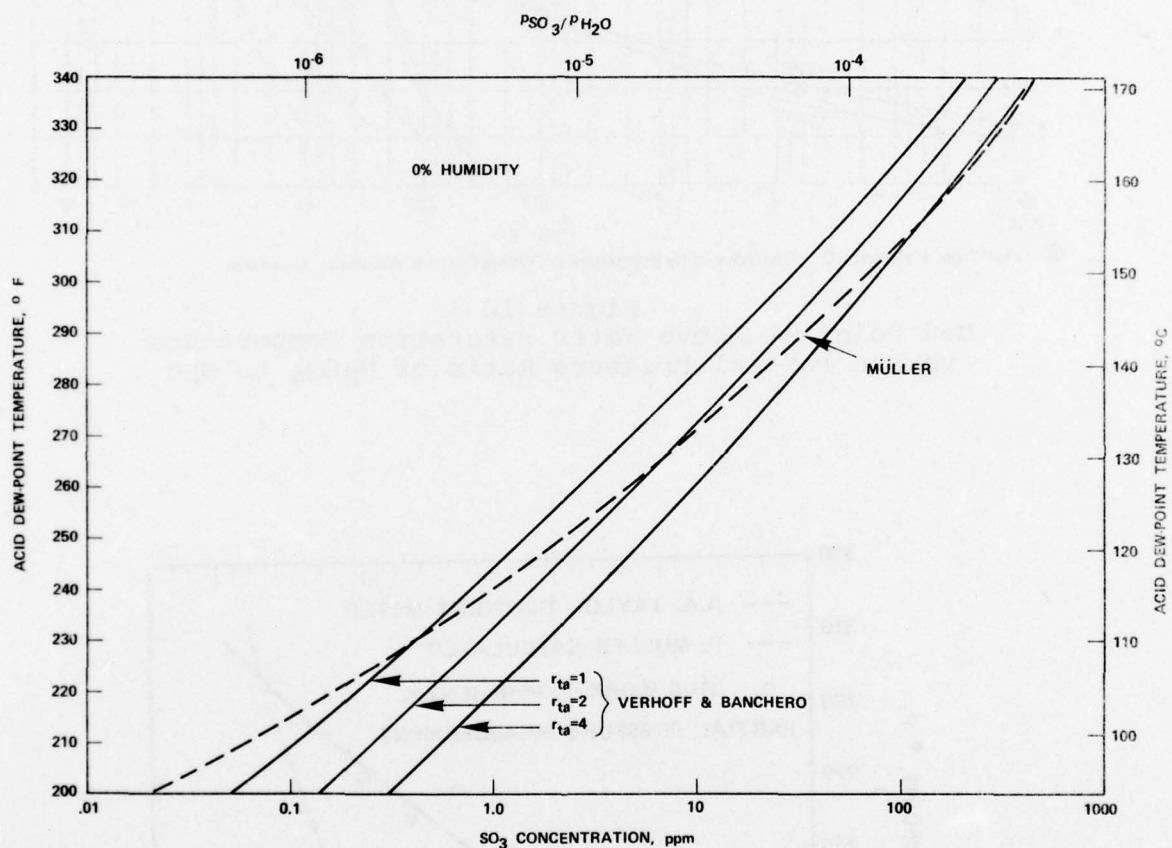


Figure 12  
Dew-Point Temperature versus  $\text{SO}_3$  Concentration  
for Müller and Verhoff & Banchemo Data



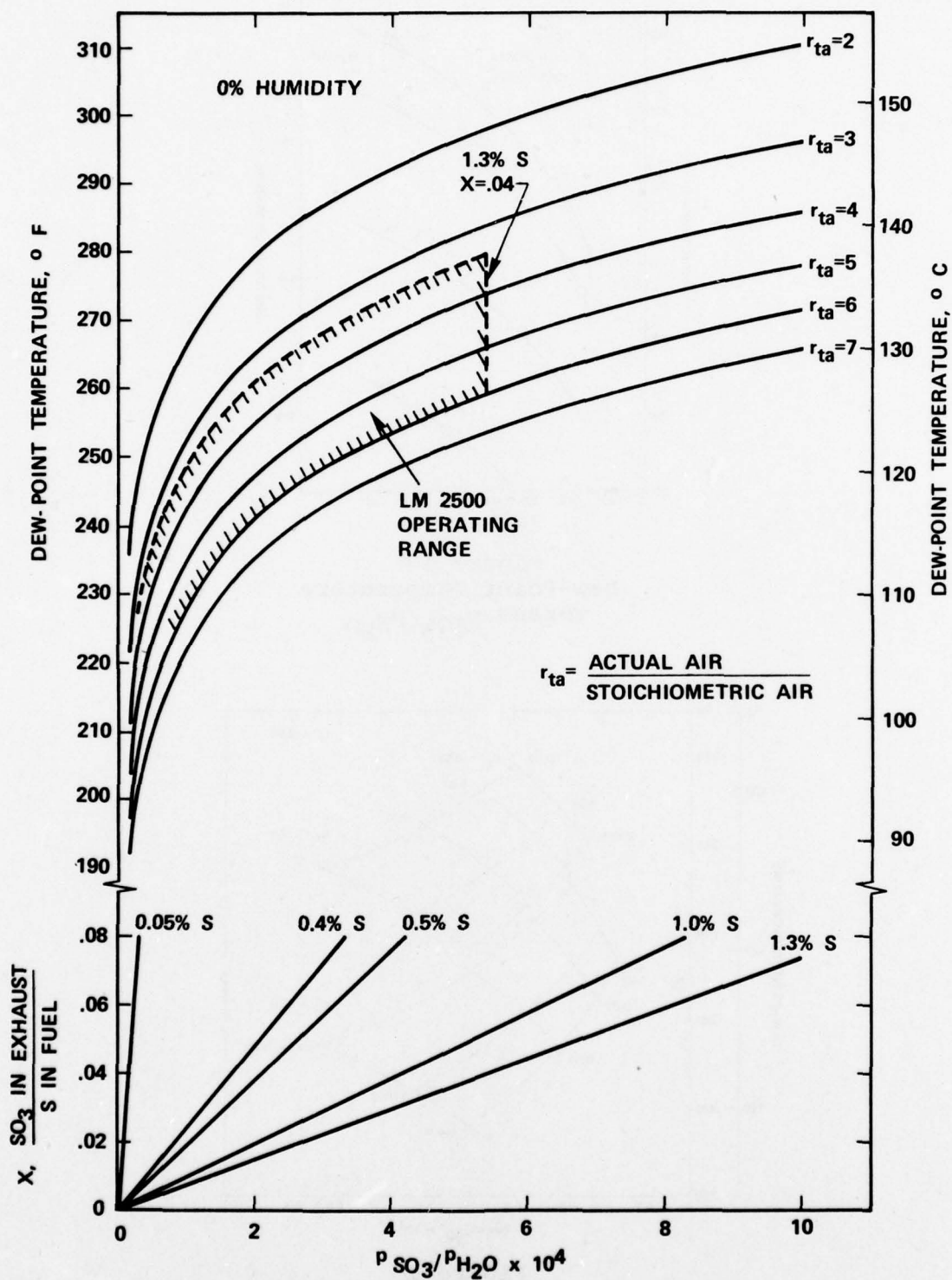


Figure 13  
Dew-Point Relationship with  $\text{SO}_3$  Concentration in Exhaust, Sulfur Content of Fuel, and Excess Air

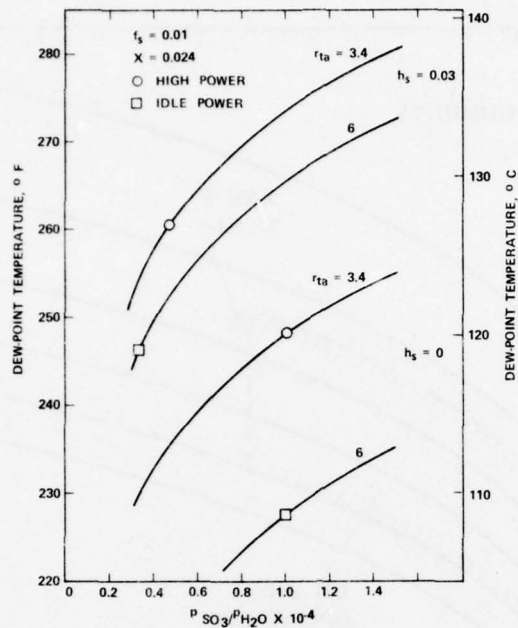


Figure 14  
Dew-Point Temperature  
versus  $p_{SO_3}/p_{H_2O}$

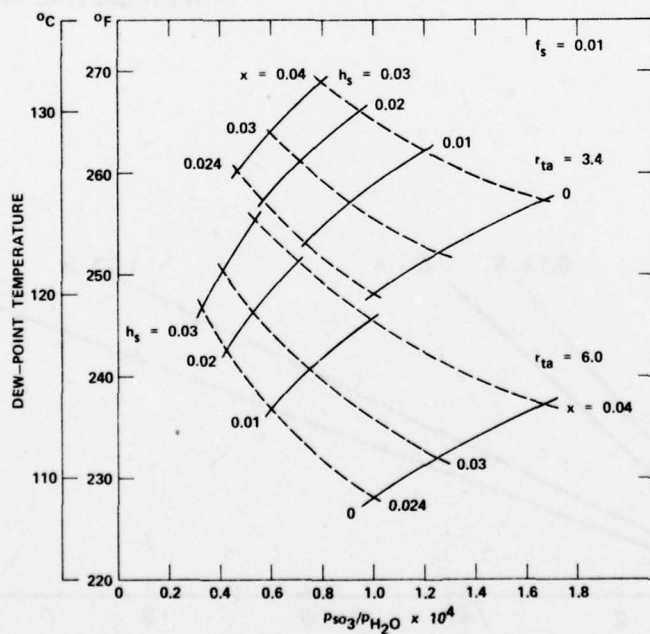


Figure 15  
Dew-Point Relationship  
with Conversion of S to  $SO_3$  ( $x$ )  
Air Ratio, ( $r_{ta}$ )  
and Specific Humidity ( $h_s$ )

C O P Y

APPENDIX A \*

CONTRIBUTION TO THE QUESTION OF THE EFFECT OF  
SULFURIC ACID ON THE DEW POINT TEMPERATURE  
OF FLUE GASES<sup>©</sup>

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SUMMARY

The dew points within the range of small sulfuric acid concentrations in flue gas are determined by utilizing thermodynamic relationships. The theoretical values obtained are compared with previously known test results.

The dew point increase in flue gas due to the presence of sulfuric acid has become a problem frequently dealt with in boiler construction bibliographies especially in the postwar period and when discussing questions of corrosion (1,26). Indeed, it has achieved a special timeliness in view of the increasing use of oil firing techniques (26,27). In the last few years, the dew point problem in engines has also been dealt with to an increasing extent (2,3,4,5). The need for this resulted from the increase in the sulfur content of diesel fuels, use of heavy oils and, not the least, from the requirement for a longer service life. The questions are unequally more difficult to solve than in boiler construction mainly owing to the rapidly changing thermodynamic state variables. This is because the equilibriums are rarely completely established owing to reaction-kinetic reasons. In addition, hardly negligible catalytic processes act to inhibit as well as accelerate the speed of equilibrium adjustment. There is dependence, for one part, on experience gained from boiler

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\*Numbers in the right margin indicate pagination in the original text.

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construction and neutralizing lubricant and fuel additives and efforts are made, usually with the help of wear measurements, to obtain some degree of insight into these conditions. In addition, reports have already been made concerning tests with dew point measuring cells on the cylinder wall (2). Further, it is noteworthy that, as a result of the special characteristic of the sulfuric acid/water vapor state diagram, high concentrated condensate already occurs with low sulfuric acid/vapor concentrations. At least in the case of cast iron, this has, however, little corrosive effect according to previous experience (6,28). A condensate with a higher aggressivity is obtained only in the vicinity of the dew point of pure steam.

The  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  formation in flue gases using sulfur containing fuels has been investigated by computational methods by Gumz (1) using equilibrium conditions. His work deals with the questionable dew point increase using the test results of Francis (7) as done quite similarly in earlier works (8) and with a limited range of sulfuric acid concentration. In addition, the same author has for about 25 years steadily generated information concerning the status of theoretical and experimental research in this area.

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The various presently still unexplained influences on the reaction to be expected in the various temperatures of the sulfur contained in the fuel leading to  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  and the question as to what extent equilibrium states are reached, are discussed in great detail by Gumz (1). The present work will investigate the dew line of a sulfuric acid/steam mixture for small partial pressure ratios.

#### EFFECT OF FOREIGN GASES

In the treatment of the sulfur/water vapor system, consideration must first be given to the fact that there are other gases in the flue gas, e.g.,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ , and nitric oxide in traces.\*

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\*Hydrochloric acid which can occur in the combustion of many fuels with chloride contents is not taken into consideration here. An investigation of the state diagram  $\text{H}_2\text{O}/\text{HCl}$  nevertheless suggests that the increase in dew point owing to hydrochloric acid is small and is probably under  $5^\circ \text{C}$  for all practical cases. This has been confirmed by measurements made by Rylands and Jenkinson (19). These authors determined that  $\text{HCl}$  in the presence of  $\text{H}_2\text{SO}_4$  only condenses in the case of the lower temperature. Cf., however (29).



These flue gas components, in contrast to generally accepted opinion to the extent that they do not react with  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , should have no noticeable effect on the condensation.

Conceivable effects of foreign gases on the vapor partial pressure are:

1. Partial pressure increase  $\Delta p_2$  caused by interaction between nonideal foreign gases and steam.
2. Partial pressure increase  $\Delta p_1$  caused by the foreign gas pressure.

The vapor pressure increase  $\Delta p_1$  caused by the pressure of foreign gases is exactly computable (9) but, however, does not need to be taken into general consideration in boiler firings owing to their low flue gas pressure.

The interaction of foreign gases is a function of their nature and temperature and is somewhat proportional to the foreign gas pressure. It can cause a partial pressure increase. According to available investigations (9), this influence can likewise be disregarded. It is in the same order of magnitude as the partial pressure increase  $\Delta p_1$  mentioned above.

Finally, the solubility of flue gas components -- these are mainly  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{SO}_2$  -- is to be considered in water. There namely occurs a dew point increase to the extent that solubility is present. The solubility of the delivered gases is slight especially when small partial pressures are present. The dew point increase can accordingly be computed by means of Henry's law. It is again negligibly small (7).

The previously available experience leads to the conclusion that practically no error can be made if the presence of the foreign gases is disregarded and the sulfuric acid/steam system is considered to be the only one present.

#### THE SULFURIC ACID/STEAM STATE DIAGRAM

##### Difficulties Occurring in Determination of the Dew Line

The vapor line of the state diagram is quite well known (10,11,12). On the other hand, only approximate statements are possible so far concerning the liquid line. The available data frequently contradict each other especially in the practical important range of small concentrations (7,13,14,15,16,17,18,19,28,30). The theory of dilute solutions (20) cannot be used because, in addition to the strong electrical dissociation of the sulfuric acid in the questionable area of small vapor concentration, a

concentrated condensate also precipitates. The last is, as initially mentioned, the special characteristic of this state diagram, cf. Figure 1.

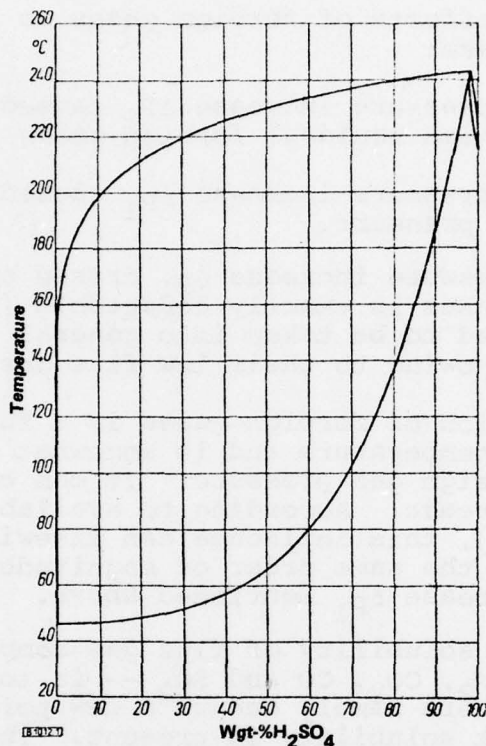


Figure 1  
State Diagram of Sulfuric  
Acid/Steam for  $P_{H_2O}$   
 $P_{H_2SO_4} = 0.10$  Atm

It is indeed possible to derive the steam partial pressures in the decisive temperature range from a number of sources (10,21) in order to compute the sulfuric acid concentration of the vapor and thereby be able to determine the dew line. Data is lacking concerning the sulfuric acid partial pressure in the range of the small values, i.e., low temperatures (cf. Figure 1).

#### COMPUTATION OF THE SULFURIC ACID/STEAM PARTIAL PRESSURES ACCORDING TO ABEL

Abel (22) succeeded, by using the third principle of chemical thermodynamics, in deriving a relationship for the sulfuric acid/water vapor pressure over the system sulfuric acid/water. This was based on a rather large number of sufficiently reliable test results of caloric

and thermal quantities of the individual components and mixture. Since the present work is based on the paper by Abel and for the sake of a better understanding, the derivation in a brief form as given by Abel is presented in detail.\* The basic thought is: In the thermodynamic equilibrium between liquid and vapor, the chemical potentials of every component must be equally large in all phases.\*\* Accordingly, in the present case,  $\mu_i'$  for the sulfuric acid vapor must be equal to  $\mu_i'$  for the liquid sulfuric acid components both referred to the liquid concentration  $c_i$ . They are dependent on the total pressure  $P$  and the temperature  $T$ .

If sulfuric acid vapor is treated as an ideal gas, which in the case of the smaller partial pressures may be admissible according to Abel, it follows that it is possible to use partial pressures in place of fugacities (23). For the pressure dependency of  $\mu_i''$ , it follows then that:

$$\mu_i'' = \mu_i''^0 + RT \ln(P_i/P_0) \quad (1).$$

In this,  $P_i$  is the partial pressure of the sulfuric acid vapor,  $R$  the general gas constant,  $T$  the absolute temperature and  $\mu_i''^0$  the so-called chemical standard potential of the pure sulfuric acid vapor with reference pressure  $P_0$  and temperature  $T$ . It is independent from the partial pressure. It is customary to have  $P_0 = 1$  atm generally as reference pressure.

In the case of an ideal mixture, computation is carried out according to Equation (1) with concentrations or partial pressures. In the case of real liquid mixtures, consideration is given to the effect of interactions by introduction of the activity concept in place of concentrations (23).

$$\mu_i' = \mu_i'^0 + RT \ln a_i \quad (2).$$

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\*Extract from the Thesis by Peter Mueller, Technical Advanced School, Hannover, 1956.

\*\*This basic thought and concepts "chemical potential," "fugacity," and "activity" are extensively described for example by G. Kortum: Introduction Into Chemical Thermodynamics, Goettingen, 1949; further by Ulich-Jost: Short Text of Physical Chemistry, Darmstadt, 1956, 9th Ed.



This relation is applied to the liquid sulfuric acid components.  $\mu_i''^0$  again refers to the standard state of the components, according to that of the sulfuric acid but still is a function only of T.  $a_i$  is, on the other hand, a function of P, T, and the concentration  $c_i$ . From the previous equation in equilibrium state, there is obtained:

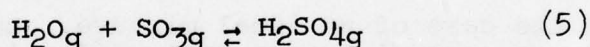
$$\mu_i'' = \mu_i' \quad (3)$$

or

$$RT \ln P_i = \mu_i'^0 - \mu_i''^0 + RT \ln a_i \quad (4)$$

The pressure dependency of the activity is negligible. Therefore, the partial pressure  $P_i$  in Equation (4) is practically independent from P.

The dependency of T requires, on the other hand, a number of conversions. The vapors from water and sulfur trioxide may react to sulfuric acid vapor according to Equation (5):



The equilibrium constants of this reaction is, in the case of an isothermal-isobar development:

$$K_p = \frac{P_{\text{H}_2\text{O}} \cdot P_{\text{SO}_3}}{P_{\text{H}_2\text{SO}_4}} \quad (6)$$

Using the assumption that the partial pressures in the pressure and temperature range in which K was experimentally determined\* are equal to the fugacities, we find that:

$$RT \ln K_p = \mu_i''^0 - \mu_w''^0 - \mu_o''^0$$

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\*Cf. for example, M. Bodenstein and M. Katayama, Z. physik. Chem. 60, 26 51, 1909



The temperature dependency of  $K_p$  is well known. For this the following is valid (24):

$$\lg K_p = -\frac{5000}{T} + 1.75 \lg T - 5.7 \cdot 10^{-4} T + 3.00 \quad (8).$$

$$\lg K_p = b_1/T + b_2 \lg T + b_3 E + b_4 \quad (9).$$

First of all, there is obtained from Equations (4) and (7):

$$RT \ln P_i = \mu_i^o - \mu_w''^o - \mu_\sigma''^o - RT \ln K_p + RT \ln a_i \quad (10).$$

If the standard potentials are taken together with the quantity

$$\Sigma \mu^o = \mu_i'^o - \mu_w''^o - \mu_\sigma''^o \quad (11),$$

it then follows that

$$RT \ln P_i = \Sigma \mu^o - RT \ln K_p + RT \ln a_i \quad (10a).$$

In this case, the temperature dependency of  $\Sigma \mu^o$ , i.e., of  $\mu_i'^o$ ,  $\mu_w''^o$  and  $\mu_\sigma''^o$  as well as those of  $a_i$  must be determined.

For the temperature dependency of the chemical potentials, the following general relation is true ((23), p. 132):

$$\left( \frac{\partial \frac{\mu_j}{T}}{\partial T} \right)_P = - \frac{\bar{H}_j}{T^2} \quad (12),$$

in which  $\bar{H}_j$  is the partial molar enthalpy of a random substance  $j$ .

When considering the temperature dependency of the enthalpy, there results:

$$\left( \frac{\partial \frac{\mu_j}{T}}{\partial T} \right)_P = - \frac{1}{T^2} \left[ \bar{H}_{j298} + \int_{298}^T \bar{c}_p^o dt \right] \quad (13),$$

in which  $\bar{H}_{j298}$  is the partial molar enthalpy at 298° K and  $\bar{c}_{pj}$  the partial molar heat.

If Equation (13) is used on the  $\Sigma \mu$  combined potentials, instead of  $\mu_j$  and is written owing to  $P = \text{constant}$ , the absolute differentials, it follows that for the dependency of the chemical potentials on the temperature:

$$\frac{d \frac{\Sigma \mu^o}{T}}{dT} = - \frac{1}{T^2} \left[ \Sigma \bar{H}^o_{298} + \int_{298}^T \Sigma \bar{c}_p^o dT \right] \quad (14)*$$

For the temperature dependency of the activity, it follows that under the assumption  $P = \text{const.}$  ((23), p. 148, Equation (152)):

$$\frac{d \ln a_i}{dT} = - \frac{\bar{L}_i}{RT^2} \quad (15).$$

$\bar{L}_i$  is, with constant pressure, the partial molar mixing heat referred to the standard state of sulfuric acid. Using the partial molar,  $\bar{c}_{pi}^o$ , for the sulfuric acid solu-

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\*Here and in the following, it will formally be disregarded that among the quantities combined to  $\Sigma X^o$  there are contained some with pure substances.

solution of the standard state and the partial molar heat  $c_{pi}$ , for the sulfuric acid components of the mixture, Equation (15) can be written

$$\frac{d \ln a_i}{dT} = - \frac{\bar{L}_i}{RT^2} = - \frac{1}{RT^2} \left[ \bar{L}_{i298} + \int_{298}^T (\bar{c}_{pi} - \bar{c}_{pi}^{\circ}) dT \right] \quad (16).$$

The integration of Equations (14) and (16) provides, if consideration is given that  $\Sigma \bar{H}^{\circ}_{298}$  and  $\bar{L}_{i298}$  are independent from the temperature, the following:

$$\frac{\Sigma \mu^{\circ}}{T} - \frac{\Sigma \mu^{\circ}_{298}}{298} = \frac{\Sigma \bar{H}^{\circ}_{298}}{T} - \frac{\Sigma \bar{H}^{\circ}_{298}}{298} - \int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{c}_p^{\circ} dT dT \quad (14a).$$

$$R(\ln a_i - \ln a_{i298}) = \frac{\bar{L}_{i298}}{T} - \frac{\bar{L}_{i298}}{298}$$

$$- \int_{298}^T \frac{1}{T^2} \int_{298}^T (\bar{c}_{pi} - \bar{c}_{pi}^{\circ}) dT dT \quad (16a).$$

If Equations (14a) and (16a) are inserted into Equation (10a), the following is true:

$$\ln p_i = \frac{1}{R} \left[ \frac{\Sigma \bar{H}^{\circ}_{298}}{T} + \frac{\bar{L}_{i298}}{T} - \frac{\Sigma \bar{H}^{\circ}_{298}}{298} + \frac{\Sigma \mu^{\circ}_{298}}{298} \right]$$

$$\begin{aligned}
& - \frac{\bar{L}_{i298}}{298} - \int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{c}_p^o dT dT \\
& - \int_{298}^T \frac{1}{T^2} \int_{298}^T (\bar{c}_{pi} - \bar{c}_{pi}^o) dT dT] \\
& - \ln K_p + \ln a_{i298} \quad (17).
\end{aligned}$$

A number of simplifications are possible here.

1. The two double integrals can be summarized taking into consideration the meaning of  $\Sigma \bar{c}_p^o$  corresponding to Equation (11):

$$\begin{aligned}
& \int_{298}^T \frac{1}{T^2} \int_{298}^T (\bar{c}_{pi}^o - c_w''^o - c_{\sigma}''^o \\
& + \bar{c}_{pi} - \bar{c}_{pi}^o) dT dT \quad (18).
\end{aligned}$$

When the quantities for pure water vapor, pure sulfur trioxide and liquid sulfuric acid in the sulfuric acid/water vapor mixture are recombined as in the case of Equation (11) (all in reference to 1 atm), we have:

$$\Sigma \mu = \mu_i' - \mu_w''^o - \mu_{\sigma}''^o \quad (19).$$

or the molar heat:

$$\Sigma \bar{c}_p = \bar{c}_{pi}' - c_{pw}''^o - c_{p\sigma}''^o \quad (20).$$

It then follows that:

$$\int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{c}_p dT dT \quad (21).$$



2. According to the Gibbs-Helmholtz Equation ((23), p. 132, Equation (108); p. 121), the following is true:

$$\Sigma \bar{H}^{\circ}_{298} = \Sigma \mu^{\circ}_{298} + 298 \Sigma \bar{S}^{\circ}_{298} \quad (22).$$

$$\frac{\Sigma \bar{H}^{\circ}_{298}}{298} - \frac{\Sigma \mu^{\circ}_{298}}{298} = \Sigma \bar{S}^{\circ}_{298} \quad (23).$$

Therein,  $S^{\circ}_{298}$  is the standard entropy (1 atm, 298° K).

3. In the terms  $\Sigma \bar{H}^{\circ}_{298}/T + \bar{L}_{i298}/T$ ,  $\Sigma \bar{H}^{\circ}_{298} + \bar{L}_{i298}$  is equal to the following enthalpies:

$$\begin{aligned} \Sigma \bar{H}^{\circ}_{298} + \bar{L}_{i298} &= \bar{H}^{\circ}_{i298} - H^{\circ}_{w298} \\ &\quad - H^{\circ}_{\sigma298} + \bar{L}_{i298} \end{aligned} \quad (24).$$

The sum

$$\bar{L}_{i298} + \bar{H}^{\circ}_{i298} = \bar{H}_{i298} \quad (25).$$

represents nothing further than the partial molar enthalpy of the sulfuric acid of concentration  $c_i$  at 298° K. Accordingly, we can write with Equation (19):

$$\begin{aligned} \Sigma \bar{H}^{\circ}_{298} + \bar{L}_{i298} &= \bar{H}_{i298} - H^{\circ}_{w298} \\ &\quad - H^{\circ}_{\sigma298} = \Sigma \bar{H}_{298} \end{aligned} \quad (26).$$

$$\frac{\Sigma \bar{H}^{\circ}_{298}}{T} + \frac{\bar{L}_{i298}}{T} = \frac{\Sigma \bar{H}_{298}}{T} \quad (27).$$

If the quantities found in (21), (23), and (27) are used, it follows that:

$$\ln P_i = \frac{1}{R} \left[ \frac{\Sigma \bar{H}_{298}}{T} - \Sigma \bar{S}^o_{298} - \frac{\bar{L}_i_{298}}{298} - \int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{C}_p dT dT \right] - \ln K_p + \ln a_{i298} \quad (28).$$

If the temperature dependency of the molar heat is developed in a power series, it follows then that it will be possible to interrupt after the first term with sufficient accuracy for the case of not too high temperatures.

There then results:

$$\Sigma \bar{C}_p = \Sigma \bar{C}_{po} + \Sigma aT \quad (29).$$

Therein  $\Sigma \bar{C}_{po}$  is the molar heat extrapolated to the absolute zero point. Now, the double integral can be solved in Equation (28):

1. Inner integral:

$$\int_{298}^T \Sigma \bar{C}_p dT = \Sigma \bar{C}_{po} T - \Sigma \bar{C}_{po} 298 + \frac{\Sigma a}{2} T^2 - \frac{\Sigma a}{2} 298^2 \quad (30).$$

2. Outer integral:

$$\begin{aligned} \int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{C}_p dT dT &= \Sigma \bar{C}_{po} \ln \frac{T}{298} + \Sigma \bar{C}_{po} \frac{298}{T} \\ &\quad - \Sigma \bar{C}_{po} + \frac{\Sigma a}{2} T - \frac{\Sigma a}{2} 298 \\ &\quad + \frac{\Sigma a}{2} \frac{298^2}{T} - \frac{\Sigma a}{2} 298 \end{aligned} \quad (31).$$

Therein can still be combined:

$$- \Sigma \bar{c}_{po} - \frac{\Sigma a}{2} 298 - \frac{\Sigma a}{2} 298 = - \Sigma \bar{c}_{p298} \quad (32).$$

$$\int_{298}^T \frac{1}{T^2} \int_{298}^T \Sigma \bar{c}_p dT dT = \left( \Sigma \bar{c}_{po} + \frac{\Sigma a}{2} 298 \right) \frac{298}{T} + \Sigma \bar{c}_{po} \ln \frac{T}{298} + \frac{\Sigma a}{2} T - \Sigma \bar{c}_{p298} \quad (33).$$

There is finally obtained from Equations (9), (28), and (33):

$$\begin{aligned} \lg P_i = \frac{\lg e}{R} & \left[ \frac{\Sigma \bar{H}_{298}}{T} - \Sigma \bar{S}^o_{298} - \frac{\bar{L}_{i298}}{298} - \right. \\ & \left( \Sigma \bar{c}_{po} + \frac{\Sigma a}{2} 298 \right) \frac{298}{T} - \Sigma \bar{c}_{po} \ln \frac{T}{298} \\ & \left. - \frac{\Sigma a}{2} T + \Sigma \bar{c}_{p298} \right] \\ & + \lg a_{i298} - \left[ \frac{b_1}{T} + b_2 \lg T + b_3 T + b_4 \right] \quad (34). \end{aligned}$$

Therewith a function is available which contains no longer any of the quantities depending on T. It can be put in the following form ( $P_i$  in torr in order to coincide with the work by Abel).

$$\lg P_i = A_i + \frac{B_i}{T} + D_i \lg T + E_i T \quad (35).$$

Therein, the constants have the following values:

$$A_i = A + A_i^* = - \frac{\Sigma \bar{S}^0_{298}}{2.30R} - 0.12 + \lg a_{i298} \\ + \frac{1}{2.30R} \left[ - \frac{\bar{L}_{i298}}{298} + 2.30 \Sigma \bar{c}_{po} \lg 298 - \Sigma \bar{c}_{p298} \right]$$

in which:

$$A = - \frac{\Sigma \bar{S}^0_{298}}{2.30 R} - 0.12 \quad \begin{array}{l} \text{independent from} \\ \text{concentration } c_i \end{array} \quad (37).$$

$$B_i = \frac{1}{2.30 R} \left[ \Sigma \bar{H}_{298} - \left( \Sigma \bar{c}_{po} + \frac{\Sigma a}{2} 298 \right) 298 \right] - b_1 \quad (38).$$

$$D_i = - \frac{\Sigma \bar{c}_{po}}{R} - b_2 \quad (39).$$

$$E_i = - \frac{\Sigma a}{2 \cdot 2.30 R} - b_3 \quad (40).$$

Abel computed these constants from a number of publications concerning the sulfuric acid/water vapor system as a function of concentration,  $c_i$ , and presented them in tabular form, cf. Table 1.



TABLE 1  
COEFFICIENTS OF VAPOR PRESSURE FORMULA  
ACCORDING TO ABEL

| $c_i$ Wgt % | $A_i$ | $(-B_i \pm 50) \cdot 10^{-3}$ | $D_i$  | $E_i \cdot 10^3$ |
|-------------|-------|-------------------------------|--------|------------------|
| 5           | +21.2 | 7.55                          | - 5.58 | + 6.7            |
| 10          | +45.4 | 8.30                          | -14.60 | +10.5            |
| 15          | +59.5 | 8.64                          | -19.90 | +13.3            |
| 20          | +66.4 | 8.66                          | -22.70 | +15.9            |
| 25          | +40.1 | 7.85                          | -12.00 | + 7.7            |
| 30          | +23.5 | 7.05                          | - 5.88 | + 5.6            |
| 35          | +11.3 | 6.50                          | - 1.10 | + 2.5            |
| 40          | - 3.8 | 5.84                          | + 4.73 | - 0.6            |
| 45          | - 4.1 | 5.66                          | + 5.03 | - 1.8            |
| 50          | - 4.7 | 5.56                          | + 5.62 | - 4.2            |
| 55          | + 3.1 | 5.59                          | + 2.71 | - 3.0            |
| 60          | + 7.0 | 5.60                          | + 1.76 | - 4.5            |
| 65          | - 5.0 | 5.00                          | + 6.38 | - 7.7            |
| 70          | - 4.8 | 4.86                          | + 6.73 | - 9.9            |
| 75          | +29.2 | 5.62                          | - 6.73 | - 1.2            |
| 80          | +47.1 | 5.98                          | -13.60 | + 2.4            |
| 85          | +45.7 | 5.54                          | -13.65 | + 5.0            |
| 90          | + 4.8 | 4.19                          | + 2.46 | - 4.8            |
| 95          | +14.6 | 4.44                          | - 1.25 | - 2.8            |
| 98.3        | +16.3 | 4.48                          | - 1.75 | - 2.6            |

DETERMINATION OF THE DEW LINE WITH THE COMPUTED SULFURIC  
ACID VAPOR PARTIAL PRESSURES

Equation (35) supplies the pertinent sulfuric acid vapor partial pressures for the acid concentrations  $c_i$  with 5 to 85 wgt % used here and temperatures ranging from 60 to 220° C.

The water vapor partial pressures (in the questionable area can be made approximately equal to the total pressures of the sulfuric acid/water vapor system) through the liquid phase were taken from various documentations for the selected temperatures and acid concentrations (10,21).

The partial pressure ratios for the selected temperatures were determined and plotted in an auxiliary diagram (Figure 2) from the computed sulfuric acid partial

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pressures and the derived total pressures. The partial pressure ratios were finally taken from this diagram for specific total pressures and temperatures.

Figure 3 represents the overall result. Here, for specific water vapor partial pressures, the dew point increase with respect to the dew point of pure water vapor is given as a function of the partial pressure ratio  $p_{H_2SO_4}/p_{H_2O}$ .

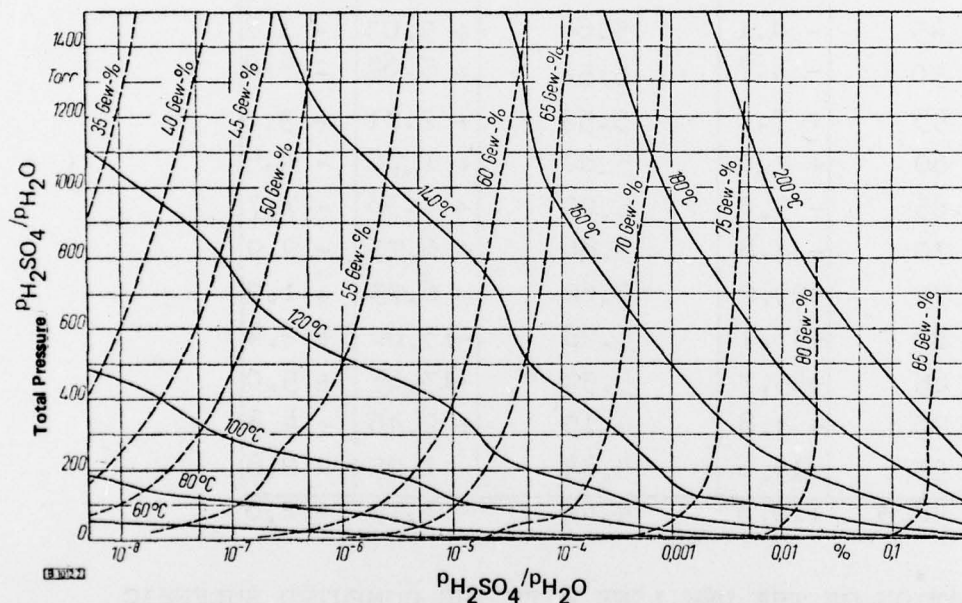


Figure 2 - Total Pressures of the Gas Phase as a Function of the Partial Pressure Ratio  $p_{H_2SO_4}/p_{H_2O}$  and the Temperature or Liquid Concentration

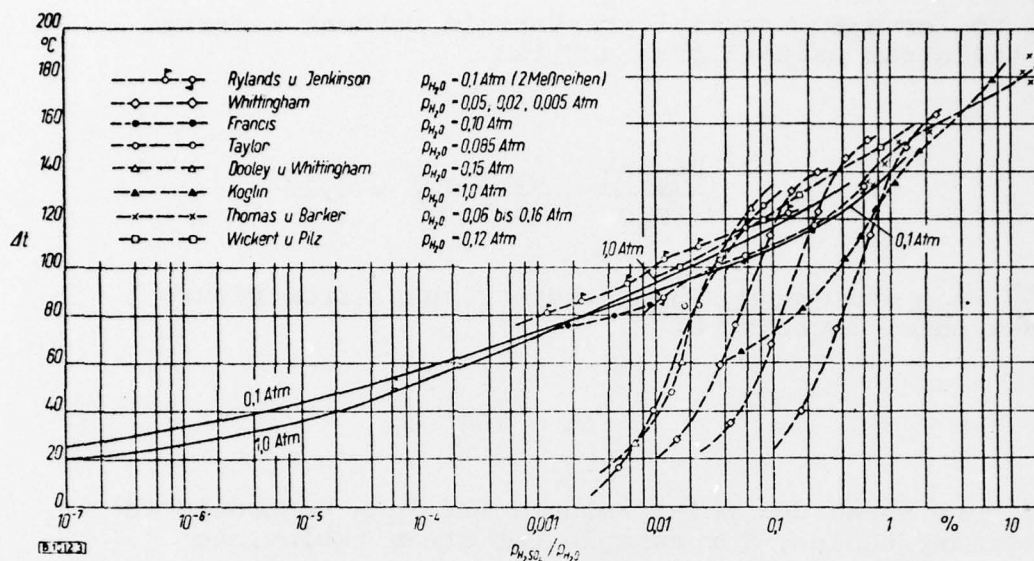


Figure 3  
Increase  $\Delta t$ , due to Sulfuric Acid Vapor, above the  
Vapor Dew Point, Comparison with Available Measurements  
 $u =$  and

Since the range encompassed here does not essentially go beyond the value of 1%, this may be set equal to the volume percentage of sulfuric acid in water vapor. For higher contents than 1%, it is to be considered that the partial pressures were used in the Abel formula in the place of fugacities.

Documentation was not available for higher vapor pressures than 2.5 atm. The pressure effect on the dew point increase is nevertheless only slight as can be seen in Figure 3.

#### COMPUTATIONAL EXAMPLE

The determination of the dew point for a steam boiler owing to the effect of sulfuric acid vapor is carried out as follows:

The content of 10 vol % water vapor and 0.01 vol % sulfur trioxide was determined for the flue gases in the dew point endangered boiler components. (The conversion from sulfur trioxide to sulfuric acid vapor takes place quite rapidly (25) so that the following is true for practical purposes:  $P_{SO_3} = P_{H_2SO_4}$ ). If the flue gas total pressure amounts to 1 atm, we then have a steam partial pressure of

$$P_{H_2O} = 0,10 \text{ Atm.}$$



The SO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> partial pressure in percent referred to the steam partial pressure is

$$\frac{P_{H_2SO_4}}{P_{H_2O}} = \frac{0.01}{10} 100 = 0.1\%$$

With P<sub>H<sub>2</sub>O</sub> and P<sub>H<sub>2</sub>SO<sub>4</sub></sub>/P<sub>H<sub>2</sub>O</sub>, there results from Figure 3 a dew point increase of

$$\Delta t = 105^\circ \text{ C.}$$

The pure steam dew point amounts for P<sub>H<sub>2</sub>O</sub> according to customary tables, for example VDI steam tables, to

$$t_w = 45^\circ \text{ C.}$$

/350

Accordingly, the total dew point

$$t = 150^\circ \text{ C.}$$

With this temperature, the condensate according to Figure 1 has a concentration of 83 wgt % sulfuric acid.

#### COMPARISON OF THE COMPUTED DEW POINT INCREASE WITH EARLIER FINDINGS

The comparison with previously known findings is advantageous,\*cf. Figure 3. Thus, the measurements made by Thomas and Barker (13) and according to Koglin (14) in the area above 1% sulfuric acid vapor check quite well with the findings of the computation. The values according to Koglin are located, on the other hand, in the case of the lesser concentrations, under the computed values.

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\*For the sake of completeness, reference is made to an American work (29) which became known shortly before printing. Therein, likewise based on Abel, the dew points are computed confirming those given here.



The deviations reported by Taylor (15), Whittingham (17), and Dooley and Whittingham (16) are similar. The reasons for this can only be surmised. Drop condensation probably appeared on the measuring surfaces of the dew point equipments so that the increase in electrical conductivity no longer coincided with the start of dew point (19). There is naturally also the possibility that the sampling and determination of partial pressure ratios was performed with some errors. This is because the dew points measured according to the same principle by Francis (7) coordinate quite well with the computed values such as the test results by Burnside, Marskell and Miller (30) (not shown in Figure 3). In addition, the data determined from corrosion measurements performed by Rylands and Jenkinson (19) and Wickert and Pilz (18) agree quite well with the computation.

In conclusion, it should be stated that the dew lines given are only valid in the case when the equilibrium state is achieved. Insofar as this is done on a practical basis is a question of condensation kinetics.

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#### NOTATIONS

For derivation of the sulfuric acid/vapor pressure formula:

##### 1. Subscripts with the symbol

- i referred to the sulfuric acid component
- j referred to any random component
- w referred to  $H_2O$
- $\sigma$  referred to sulfur trioxide
- p with constant pressure
- 298 ref. to standard temperature of 298° K (25° C)
- o ref. to absolute zero (0° K) except with pressure  $P_o$

##### 2. Superscripts with the symbol

- o component located in standard state, i.e.,  
with gases: 1 atm and ideal behavior  
liquids: 1 atm, stable state form  
mixed phases: 1 atm, activity of observed component equal to 1
- ' liquid phase (can also be missing)
- " gas phase
- $\bar{x}$  quantity x is a partial molar quantity

### 3. Symbols

|   |  |
|---|--|
| $a_i$   | activity of the sulfuric acid component in the liquid phase  |
| $b_1 b_2 b_3 b_4$                               | constants of Equation (9)  |
| $c_p$   | molar heat with constant pressure  |
| $c_i$   | concentration of sulfuric acid in liquid phase in wgt %  |
| $H$   | molar enthalpy   |
| $K_p$   | equilibrium constants of the reaction referred to the partial pressures  |
| $\bar{L}_i$                                     | partial molar mixing of heat of sulfur acid components in water  |
| $P$   | total pressure of system   |
| $P_o$   | ref. pressure = 1 atm  |
| $R$   | general gas constant (not to be confused w/individual gas constant which has same symbol in technical biblio.) |
| $S$   | molar entropy  |
| $T$   | absolute temperature of system ( $^{\circ}K$ )   |
| $\Sigma X^o = X_i^{'o} - X_w^{''o} - X_o^{''o}$ | } combination of certain quant. X corresponding to the subscripts  |
| $\Sigma X = X_i^{'o} - X_w^{''o} - X_o^{''o}$   |  |
| $\alpha$  | temp. coef. of molar heat acc. to Eq. (29)   |
| $u$   | chemical potential   |

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APPENDIX B  
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